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(54) Title: PROCESSES AND APPARATUS FOR MAKING MULTILAYER PLASTIC ARTICLES

(57) Abstract

Processes and apparatus for making multilayer plastic articles, wherein the articles are comprised of a number of discrete and substantially continuous layers adjacent critical surfaces of the articles, which display a substantial uniformity of composition with respect to property-affecting constituent materials adjacent such surfaces, or which have discrete and substantially continuous layers of these materials within a selected layer order adjacent critical surfaces of the articles.

PROCESSES AND APPARATUS FOR MAKING MULTILAYER PLASTIC ARTICLES

The present invention relates to multilayer plastic articles and to processes and apparatus for making such articles.

5   It has been appreciated previously that articles comprising overlapping layers of diverse thermoplastic materials could realize a combination of properties which could not be realized otherwise, except by the synthesis of an entirely new material or the use
10   of a prohibitively expensive existing material. A number of processes and apparatus have accordingly been developed or suggested for making moldable, three-dimensional multilayer plastic articles of this type.

15   Exemplary of these known processes and apparatus are those disclosed in United States Patents No. 4,525,134 to McHenry et al., 3,339,240 to Corbett, 4,410,482 to Subramanian, and 3,716,612 to Schrenk et
20   al, and in European Application 0278403 (Mitsubishi Gas Chemical Company Inc.).

25   complexity, materials limitations, limitations on the

number or arrangement of layers, limitations on the
shapes of articles which can be made thereby, and so
forth. None of these known processes and methods,
additionally, are disclosed or suggested to be suitable
for use with multicavity injection molding or in the
5   context of a multicavity injection molding process, or
more particularly for multicavity injection molding
wherein differing mold geometries are involved.

The processes and apparatus of the present
10 invention are not so limited, however. The moldable
articles of the present invention comprise discrete and
substantially continuous layers of a plurality of
diverse thermoplastic materials, and can be produced
with a substantial uniformity of composition in a
15 multicavity injection molding process, even where
differing mold geometries are involved and where one of
the materials is present only as a minor component (less
than about 15 percent by volume). These layers may also
20 be prearranged in a selected layer order, which selected
layer order will be preserved in the molded article.

The novel and improved processes and apparatus
for making such articles begin with the coextrusion of
25 discrete, generally planar layers of first and second
diverse thermoplastic materials in a first composite
stream. In one set of processes and apparatus, the first
composite stream is thereafter formed directly into a
desired configuration with certain desirable qualities
30 by some process other than thermoforming, such as by
injection molding, injection blow molding, extrusion
blow molding, displacement blow molding, compression
molding, or transfer molding. In another group of
processes and apparatus contemplated by the present
invention, the first composite stream is manipulated to

form a second composite stream having an increased
number of discrete, generally planar layers of the first
and second materials compared to the first composite
stream, and the layered second composite stream is then
formed into a desired configuration, for example by one
of the above-mentioned processes.

Fig. 1 is a schematic of an apparatus of the
present invention for injection molding multilayer
plastic articles.

Fig. 2 is a schematic illustration of the
formation of a second composite stream from a first
composite stream.

Fig. 3 is an exploded view of an apparatus for
forming a second composite stream from a first composite
stream as schematically illustrated in Fig. 2.

"Figures 4A and 4B are photomicrographs of
cross-sections of cans molded from brown and white
polypropylene, with the cross-sections being taken near
the lip of a respective can and comparing the uniformity
of layer thicknesses and evenness of layer distribution
which may be achieved by using a commercial Ross
interfacial surface generator (Fig. 4A) and the ISG of
Fig. 3 (Fig. 4B).

Figures 4C (Ross) and 4D (ISG of Fig. 3) make a
similar comparison of cross-sections from the middle of
a can.

Figures 4E (Ross) and 4F (ISG of Fig. 3)

Fig. 5A schematically depicts an apparatus for reducing the exposure of layer edges of a layered stream.

Fig. 5B depicts the inlet side of the apparatus
5   of Fig. 5A.

Fig. 5C depicts the outlet side of the apparatus of Fig. 5A.

10   Fig. 6A is a photomicrographic view of a section of a layered melt stream before passing through the apparatus of Fig.'s 5A-C.

Fig. 6B is a photomicrographic view of the
15 section of Fig. 6A, after passing through the apparatus of Fig.'s 5A-C.

Fig. 7A is a photomicrograph in cross-section of an article produced by transfer molding a melt stream
20 which is as depicted in Fig. 6A.

Fig. 7B is a photomicrograph in cross-section of an article produced by transfer molding a melt stream which is as depicted in Fig. 6B.

25   Fig. 8 is a depiction of the location of cross-sectional micrographs taken with respect to transfer molded parts in a simulation of multicavity injection molding.

30   Figures 9A-H presents the series of micrographs whose locations are noted in Fig. 8.

Figures 10A-C shows a transfer molding apparatus as used to demonstrate the present invention.

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Figures 11A and 11B are cross-sectional
photomicrographs taken along orthogonal axes of an
article of the present invention constructed as set
forth in Example 2 below."

5   Referring now to Figures 1-11, and more
particularly to Fig. 1, an apparatus 10 of the present
invention is schematically illustrated. Extruders 12,
14 and 16 of Fig. 1 are sources of first, second and
third diverse heat plastified thermoplastic materials,
10 respectively. The depiction of only three extruders as
in Fig. 1 does not negate the presence and use of
perhaps additional or even fewer extruders or sources of
thermoplastic materials, where other or fewer materials
are sought to be incorporated into layers of a
15 multilayer article to be formed. Additional materials
and layers of materials may be required, for example,
where two materials or two at least partially
incompatible materials joined by a third compatibilizing
20 material cannot by themselves impart the desired
improvement in properties to the articles to be formed.

25

30

It should be noted parenthetically that the
term "diverse" is intended to suggest only some
measurable distinction between such "diverse" materials.
This distinction may be of a chemical nature, a physical
nature, or in the nature of a difference in color,
5   appearance or optical effect. It is not necessary that
one material be, for example, polyethylene while a
second, "diverse" material is polypropylene. Nor is it
necessary that the materials themselves comprise but a
10   single identifiable species, so that a mixture of
polyethylene and polypropylene could comprise a
"thermoplastic resinous material" for purposes of this
invention, and would be diverse from polyethylene or
polypropylene individually.
15
Means for generating and controllably or non-
randomly arranging layers of the first, second and third
materials in a first composite stream is schematically
depicted in Fig. 1 and comprises in a preferred
20   embodiment a coextrusion feedblock apparatus 18. A
preferred coextrusion feedblock apparatus for generating
and arranging layers of the first, second and third
materials in a first composite stream is as disclosed in
United States Patent No. 3,557,265 to Chisholm et al. or
25   as disclosed in United States Patent No. 3,884,606 to
Schrenk et al.

The present invention relies upon the
arrangement of the extruders and the feedblock apparatus
30   to control the thicknesses, distribution, and
arrangement of layers of the various materials to be
included in the first composite stream. In this way, it
is a relatively simple matter in the context of the
teachings of the coextrusion art:

1) to order the layers of the first, second and third materials, for example, within a first composite stream so that the third material may be initially advantageously placed;

5   2) to distribute the materials substantially evenly in the composite stream so that the distribution of the layers in the finished article will be relatively even also and the article will display a substantial uniformity of composition with respect to at least the

10   layers of property-affecting materials adjacent a critical surface of the article; and/or,

3) to select a layer thickness for layers of each of the various materials so that subsequent

15   manipulations of the emerging composite stream do not cause the layers of the various materials in the ultimately desired configuration to depart from a substantially continuous nature.

20   By "substantially continuous," it is meant only that the individual layers have significantly more of the character of a continuous layer extending throughout and around the walls or boundaries of an article, and

25   more particularly adjacent a critical surface of the article, than any partial lamellae which would be created in accordance with or suggested by the teachings of the prior art.

30   A "critical surface" refers to a surface of the article which will be subject to various stresses or wherein the properties which are sought to be enhanced by a lamellar construction will be desired. Where the

with respect to a particular gas or solvent, for

example, a critical surface would correspond to any
surface which is expected to contact that gas or solvent
and to form a barrier to permeation of the gas or
solvent therethrough.

5   We consider that no more than about 10 percent
of these layers of the property-affecting materials of
interest should have an interfacial surface area to unit
thickness ratio of less than 10:1 to realize the
benefits and advantages of our invention, although
10   preferably and typically the dimensions and thicknesses
of layers created by the processes of our invention will
be such that multilayer articles produced thereby have
properties and a cross-sectional microscopic appearance
approaching those of a thin, flat coextruded sheet.
15   Thus, the interfacial surface area to unit thickness
ratio for layers of the property-affecting materials of
interest adjacent a critical surface of an article will
preferably be at least 100:1, and most preferably at
20   least 1000:1.

          The referenced interfacial surface area to unit
thickness ratio is calculated by resolving a layer into
an element of length l and of width w, with a unitary
25   thickness. Thus, where a layer is observed to
approximate in interfacial surface area a rectangle of
length l_1 and width w_1, and is observed to have an
average thickness t, $l=l_1/t$ and $w=w_1/t$ approximately.
The amounts l and w can be thought of as expressing the
30   degree of extensiveness of a given layer in a direction
compared to other layers of a like thickness. The
interfacial surface area to unit thickness ratio of a
given layer would be represented by the product
$lw=(l_1/t)(w_1/t)=l_1w_1/t^2$.

In considering how this ratio applies to
describe our layers, one may refer to the cross-
sectional photomicrographs of Fig. 11A. These
photomicrographs depict the cross-sections of a specimen
from an article molded as described in Example 2 below.

5   The specimen was cut to expose cross-sections in the
direction of flow during mold-fill and in a direction
perpendicular thereto. The thickest layer which is
clearly visible in Fig. 11B can safely be assumed to
encompass an interfacial surface area at least equal to

10   the product of the width of photomicrograph A and the
distance from the right edge of B to where the white
material appears in the midst of the layer, or at least
equal to about $3.5 \times 1.5 = 5.25$ square inches (33.87

15   cm^2) on the scale of the photomicrographs. On the same
scale, the thickness of the layer appears not to exceed
about .2 inches (.5 cm) on the average, so that the
interfacial surface area to unit thickness ratio for
this layer appears to be at least about

20   $5.25/(.2)^2 = 131.25$.

Further, one can discern a number of layers
immediately above the layer just discussed which appear
to be fully continuous over the widths of both

25   photomicrographs, and yet have a thickness substantially
less than that of the thickest layer so that the
interfacial surface area to unit thickness ratio for
these substantially parallel layers should be much
greater than the about 131.25 ratio seen for the

30   thickest layer. For example, the layer immediately above
the thickest layer would appear to have an interfacial
surface area of at least about $3.5 \times 3.5 = 12.25$ square

appear to be on the order of at least $(3.5 \times 3.5)/.05^2 = (l_1 w_1)/t^2 = 4900$.

Given that none of the layers in Fig. 11 exhibit large fluctuations in thickness, it appears likely that the layer above the thickest layer extends continuously for a still greater distance in both directions implicated in photomicrographs A and B, without dramatic corresponding increases in thickness such as would have the effect of decreasing the overall surface area to thickness ratio of the layer. Rather, the photomicrographs suggest that the full extent of the layer as seen on the scale of the photomicrographs may be significantly greater than 12.25 square inches (79.0 cm^2) while the average thickness of the layer would be the same or less than the 0.05 inches (0.127) cm) used above, so that the layer were it to be measured in full would have an interfacial surface area to unit thickness ratio correspondingly greater than even 4900.

Also by way of definition, a "substantial uniformity of composition" as used herein refers to the deviation of the local composition ratio within a wall of the molded article from the average composition ratio of the article as a whole, the latter ratio being determined by the ratio of feed rates of individual polymer components to the processes of the present invention. The local composition ratio refers to the composition ratio of a specimen from adjacent a critical surface of the molded article, the specimen being derived from within the composite stream in its desired configuration and having dimensions of at least the local thickness of the molded article in all directions.

A "substantial uniformity of composition"
exists where local composition ratios along a critical
surface of the article do not vary by more than 20
percent, and preferably no more than 10 percent, from
the average composition ratio. In general terms, this
5   substantial uniformity of composition is important in
achieving a uniformity of properties along a critical
surface of the article in the desired configuration.

Returning to a discussion of the coextrusion
10   feedblock apparatus 18 illustrated schematically in
Figure 1, it will usually be desirable to employ a 2, 3,
4 or 5-layer feedblock apparatus where only the first
and second materials are used, so as to create for
example with the 5-layer apparatus an ABABA-type layer
15   structure in the first composite stream, or where first,
second and third materials are used, creating an ABCBA-
type structure for instance. Where such a 2,3,4 or 5-
layer feedblock apparatus is used, it is thought that a
20   feedblock such as is disclosed in United States Patent
No. 3,577,265 to Chisholm et al. should be satisfactory,
and a number of total layers of the first and second, or
of the first, second and third materials in excess of
the 2, 3, 4 or 5 respectively created thereby may be
25   created by employing means for manipulating the first
composite stream from coextrusion feedblock apparatus 18
to form a second composite stream which has an increased
number of layers of the first and second, or of the
first, second and third materials compared to the first
30   composite stream. This manipulation is characterized in
Figure 1 as "Layer Multiplication."

ream to form a second composite stream preferably
includes means for dividing the first composite stream

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to form a plurality of substreams which collectively
comprise an increased number of layers of the first and
second, or of the first, second and third materials
compared with the first composite stream, and means for
combining the substreams to form the second composite
5   stream. The formation of the second composite stream
from the first composite stream and a preferred
apparatus for accomplishing this formation are
schematically shown in Figures 1 and 2, and shown in
10   more detail in Fig. 3.

         Referring now to Fig. 2 specifically, a
schematic of the creation of additional layers of the
first and second materials of the first composite stream
15   for the second composite stream is illustrated, and
shows that a melt stream comprised of layers 19a and
19b, respectively, of the first and second materials in
an ABA-type construction is divided in a plane which is
generally perpendicular to the layers of the melt
20   stream, then flattened and recombined by means for
stacking the substreams. "Stacking" the substreams in
this manner refers to the recombination of the sub-
streams in a direction which is generally perpendicular
to the layers of the substreams, such that the combined
25   layers of the substreams are substantially parallel to
one another.

         An apparatus for dividing the first composite
stream to form a plurality of substreams and to
30   recombine these substreams to form a second composite
stream by stacking the substreams is shown in Fig. 3.
In Fig. 3 it can be seen that, at the entrance 20 of the
interfacial surface generator (ISG) depicted in Fig. 3 a
first composite stream represented by the arrow 22 is
divided by a blade or thin wall section 24 which is

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generally perpendicularly oriented with respect to the layers of the first composite stream.

A substream 26 of the first composite stream ascends a generally rectangular-shaped, sloping passageway 28 to the left of blade 24, while a second substream 30 of the first composite stream descends a passageway 32 to the right of blade 24 which is similar in shape to the passageway 28 but which slopes downward.

Substreams 26 and 30 are then essentially stacked by passageways 34 and 36, with passageway 34 forcing substream 26 back to the right and passageway 36 forcing substream 30 to the left. The layers are kept from mixing during these lateral movements by a blade or thin wall section 38 which is oriented generally parallel to the layers of the substreams 26 and 30.

Substream 26 is then flattened and forced downward in a passageway 40 while substream 30 is flattened and forced upward in a passageway 42, the substreams 26 and 30 again being prevented from mixing by a thin wall section 44. The substreams 26 and 30 are then allowed to recombine to form a second composite stream which has a greater number of layers of the first and second materials than the first composite stream.

By using an apparatus such as is depicted in Figures 2 and 3, or by using other conventional ISG's such as sold by Charles Ross & Son Company, P. O. Box 2200, Hauppauge, N.Y., USA 11787 or as described in United States Patent No. 3,195,865, a great many layers

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An equivalent number of layers might be formed merely by using a larger coextrusion feedblock apparatus, such as disclosed in United States Patent No. 3,884,606 to Schrenk et al., and the coextrusion feedblock apparatus of that patent is preferred over

5   more conventional feedblock apparatus employing a linear feedblock where a fairly large number of layers is to be generated without the use of the sort of apparatus depicted in Figures 2 and 3.

10   Under such circumstances, an apparatus as disclosed in United States Patent No. 3,884,606 should be less likely to contribute to a significant proportion of the layers at the edges of the first or second

15   composite stream becoming discontinuous on forming the stream into a desired configuration.

As a rule, though, as compared to the use of a coextrusion feedblock apparatus alone, a standard 2, 3,

20   4 or 5-layer coextrusion feedblock apparatus is preferably used in combination with one or more ISG's as described above. As for selecting the type or types of ISG's for a particular application, it should be observed that the various known ISG's which could be

25   used will generally distort the composite stream from the coextrusion feedblock apparatus to different degrees.

The ISG of Figures 2 and 3 generally produces

30   less distortion of the nonrandomly arranged composite stream emerging from the coextrusion feedblock apparatus, for example, and a greater uniformity in layer thicknesses within the second composite stream and in an injection molded article having a desired configuration than do the commercially available four

channel Ross elements with respect to layers of a given
material. This difference is particularly illustrated
in Figure 4A-F, which shows a series of comparative
photomicrographs of cross-sections of a wall of a can
which has been injection molded from layers of brown and
5   white polypropylene, using ISG's of the type shown in
Fig.3 and the Ross ISG's.

A lesser distortion of the first composite
stream in the creation of the second composite stream
10 should typically mean a lesser departure from the
properties and characteristics desirably imparted to the
first composite stream in the coextrusion feedblock
apparatus 18, and a greater likelihood of those charac-
teristics being transferred through to the finished
15 article with fewer variables being involved in trying to
achieve a desired configuration of that article having
those properties.

Determining when one might desire to use a
20 coextrusion feedblock apparatus only or in an
ISG/feedblock combination with a particular combination
of ISG's depends on a number of considerations,
including for example:

25
1) whether the equipment is to be dedicated to
a particular application for a sufficient length of time
that the decreased flexibility involved in using a
feedblock apparatus alone is not counterproductive in an
30 overall sense;

2) whether the application is of such a
demanding nature that the distortion involved in the

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increased fabrication costs associated with a complex
feedblock apparatus is offset;

3) the availability of space and equipment, and
specifically as to the latter, the availability of an
5   appropriate feedblock apparatus;

4) the degree of distortion introduced with
each ISG, within the limits imposed on the length of the
ISG's by degradation and space concerns; and

10

5) whether a degree of degradation may be
tolerated with respect to certain materials in the
interests of lesser layer distortion through the ISG's.

15   The significance of greater layer uniformity
being transferred through to the finished article by the
careful selection of appropriate layer generation,
arrangement and/or multiplication means lies in part, it
is believed, in the optimization of those properties
20   which are enhanced by a lamellar construction.

It has generally been noted that for a given
system of diverse thermoplastic resinous materials in a
given mold geometry, an optimum mix of properties may
25   correspond roughly to a given number or range of numbers
of layers of such property-affecting materials. Where
this number of layers is large, or the wall thickness
locally small adjacent a critical surface of the
article, it may be difficult to achieve this optimal
30   blend of properties throughout an article.

Further, it is generally true that all other
things being equal, the larger the number of layers
across a cross-section of the wall of an article, the
greater the improvement in those properties which are

enhanced by a lamellar construction, so long as the
layers are substantially co-continuous across that
cross-section of the article.

A significant variation in the layer
thicknesses of a given property-affecting material
across such a cross-section can be viewed as effectively
reducing the number of layers of such a material as some
layers approach a discontinuous nature, and while the
effect of the difference in the amount of distortion
involved in using one type of ISG as opposed to another
might be small in one application, for other systems the
effect might be sufficiently significant to warrant a
preference for one type or one particular combination of
ISG's.

Whether the desired number of layers is created
in a second composite stream by the combination of a
coextrusion feedblock apparatus and an ISG or a series
of ISG's, or in a first composite stream merely by a
coextrusion feedblock apparatus, a resulting layered
melt stream is molded into a desired configuration by
means for accomplishing this function, or the stream may
first be passed through what has for present purposes
been termed a "symmetricizer".

A "symmetricizer" is a device which has been
developed for reducing the number and extent of exposed
layer edges in a layered melt stream including diverse
thermoplastic resinous materials prior to forming the
stream into a desired configuration by injection
molding, compression molding, transfer molding,

the exposure of layer edges in that desired
configuration of an article.

A symmetricizer might appropriately be employed
where the properties which are sought to be enhanced by
5   a lamellar construction could be significantly adversely
affected by the exposure of a number of layer edges at a
surface of the finished article to external influences,
and where because of the mold geometry, method of
forming the article, the materials used, etc., such
10   exposure is likely to occur. One example of such a
situation might be where a saponified ethylene-vinyl
acetate copolymer is being used to provide an oxygen
barrier to an article produced in accordance with the
15   present invention, where upon exposure to moisture in
the article's environment a loss in barrier and
mechanical properties can be expected.

In general the symmetricizer is designed to
20   reduce the exposure of layer edges in a layered melt
stream by dividing the stream into two or more
substreams having layers of thermoplastic materials, and
then combining these substreams such that a majority of
the layers of one of the substreams are generally
25   angularly oriented with respect to a majority of the
layers of a second substream.

What is generally intended in the operation of
the symmetricizer device of this invention is first, to
30   dispose some of those layer edges which would otherwise
initially come into contact with the walls of a mold at
a perpendicular angle and freeze in such an orientation
so that they initially contact the walls, if at all, at
a significantly greater or lesser angle. Secondly, it
is thought that placing the majority of the layers of

one of the substreams at an angle with respect to the
majority of the layers of a second substream will create
a tendency of the layer edges to enfold one another.

In the enfolded structures, the greater portion
5   of layers of the first, second and third materials will
preferably lie generally parallel to a critical surface,
but with the layer edges of sensitive layers being
interwoven and overlapping rather than intersecting a
critical surface of the article.
10

Some degree of layer distortion is occasioned
by this manipulation of the stream to be molded or
otherwise formed into a desired configuration. The
effects of this layer distortion are a cost associated
15   with a reduction of exposed layer edges in the article,
and it is expected that this cost will need to be
considered in determining whether the use of a
symmetricizer may be appropriate for a given
application.
20

In multicavity injection molding it may not be
necessary to employ an apparatus for reducing the
exposure of layer edges where the use of the article and
the materials used in constructing the article might
25   otherwise suggest the advisability of such an apparatus,
in that the flow of the layered stream through runners
and gates will usually sufficiently randomize the layers
of the stream to reduce the number and/or extent of
30   exposed layer edges in both the layered stream and the
finished article. Nevertheless, even in multicavity
injection molding a symmetricizer may still be of some

symmetricizer in any particular set of circumstances

might more suitably be judged on a case by case basis.

A preferred symmetricizer is shown in Figures
5A-C , and comprises a plurality of inlet ports 46 and a
5   plurality of outlet ports 48, the outlet ports 48 being
generally divided into central outlet ports 48a and
peripheral outlet ports 48b. Inlet ports 46 are
generally rectangular in shape, and preferably have a
long dimension which is parallel to the layers of first,
10 second and third materials of the first or second com-
posite stream which are received therein. The internal
channels 50 of the symmetricizer which correspond to
inlet ports 46 and outlet ports 48 are preferably of a
constant rectangular configuration which matches that of
15 corresponding inlet ports 46 and outlet ports 48, and
preferably provide an incrementally consistent change of
orientation from an inlet port 46 to an outlet port 48,
as suggested in Fig. 5A. As shown, outlet ports 48a
20 associated with substreams of the first or second
composite stream passing therethrough are oriented
substantially at a 90° angle with respect to one
another, as are outlet ports 48b.

25   An illustration of the transformation worked by
the symmetricizer of Fig. 5A-C may be seen in Fig. 6A
and 6B, which depicts cross-sections of a layered melt
stream of brown and white polypropylene prior to and
following passage through a symmetricizer configured as
30 in Fig. 5. An indication of how the reduction in
exposed layer edges accomplished by the symmetricizer
can translate through the formation step to a finished
article can be seen in Fig. 7A and 7B, which depicts
photomicrographs of cross-sections of the walls of cans
injection molded from the same brown and white
polypropylene with and without the

symmetricizer. As may be seen from Figure 7A and 7B, the symmetricizer appears to have reduced at least the extent of layer edges which are perpendicular to a surface of the can, if not the number of such edges.

5   Referring back to Fig. 1, it can be seen that the first or second composite stream is thereafter molded into a desired configuration by a process other than thermoforming, such as by the preferred injection molding process or by compression molding, transfer
10 molding, injection blow molding, displacement blow molding or extrusion blow molding.

    The preferred manner of forming a first or second composite stream of the present invention into a
15 desired configuration would, as previously suggested, involve some sort of injection molding. Coextrusion, though, has generally been developed as a continuous process, while injection molding is an intermittent
20 process. One possible way in which the invention could be practiced with both processing methods integrated therein would use accumulators and valves to direct flow to one accumulator during the molding cycle of another.

25   Another possible way would be to use reciprocating screw injection of each of the first and second or first, second and third materials through the coextrusion feedblock apparatus, so that intermittent flow for injection molding is established before and
30 during layer generation and arrangement into a composite melt stream, rather than afterwards.

    A particularly preferred manner of forming a

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had been demonstrated in United States Patent No.
3,716,612 that a lamellar construction could be
transferred from a layered melt stream into a finished
article after injection molding, it was not known
whether such a lamellar construction could be maintained
5   throughout the full extent of a multicavity mold where
one of the layered components was present as a minor
phase (at less than about 15 percent by volume, for
example). By the present invention, a lamellar
10 construction can be maintained throughout the extent of
a multicavity mold for even minor components within a
lamellar melt stream.

     Examining the operation of the apparatus
15 described above in performing the processes of the
present invention for making moldable multilayer plastic
articles, one potential application would be in the
making of plastic containers for carbonated beverages.
Such containers have in the past been made of
20 polyethylene terephthalate (PET), which forms a fairly
good barrier to the loss of carbon dioxide from the
beverage. In an effort to lengthen the shelf life of
these beverage containers, especially for smaller such
containers, one might wish to create a multilayer
25 structure incorporating layers of PET and of a resin
with a better barrier to CO_2, such as an ethylene vinyl
alcohol (EVOH).

     In considering how one might achieve the
30 benefits of the present invention with a PET/EVOH system
as the first and second diverse thermoplastic materials,
one approach that is presently foreseen would first
match the viscosities of the PET and EVOH over a range
of nondegradative temperatures within the general limits
suggested by the coextrusion art, given the sensitivity

of the system to discontinuities in layers and similar
such considerations. For purposes of the present
invention, generally materials having viscosities that
differ by no greater than a factor of five can be
appropriately used together in the present invention,

5   and even greater viscosity mismatches might be
tolerated, although the upper limits on this are not
presently known.

The next step would be to consider whether PET
10 and EVOH are sufficiently self-adhering to possess
adequate structural integrity for a carbonated beverage
container. If not, a third, compatibilizing material
needs to be selected to adhere layers of the PET and
EVOH together in the finished article.

15

A variety of compatibilizing materials are
known, and may be advertised as adhering to both PET and
EVOH, or may be known to adhere to both. Of those
materials which emerge as potential candidates for use

20 as the third material, one would select materials for
further evaluation which could be matched to the PET and
EVOH rheologically within the nondegradative temperature
range established earlier, and which would not

25 themselves degrade at the temperatures of interest.

The candidates could then be coextruded with
the PET and EVOH, and peel tests conducted of the
resulting structure to determine which of the candidate

30 materials provided adequate adhesion and the amounts of
such materials necessary to provide such adhesion.
Taking into account such things as the materials cost

and the availability of the material, a selection would
then be made of the third material to be used.

The first, second, and third materials would
then be melt coextruded with proper temperature controls
5   on the source extruders to match the rheologies of the
various materials, and with the second and third
materials generally being used in the minimum amounts
thought necessary to achieve a desired barrier, since
the second and third materials will typically be more
10 expensive than the first material whose purpose will
normally be primarily of a structural nature. In this
regard, it has been found that the second material can
typically comprise less than about 10 percent by volume
15 of the first composite stream without the layers of this
material becoming discontinuous to an unacceptable
degree when employed in a process and apparatus of the
present invention.

20 One or more ISG's or a different feedblock may
then be employed, as discussed earlier, to increase the
number of layers. Testing of the articles produced by
the process for various numbers of ISG's should
establish whether the desired barrier can be achieved
25 for the materials and levels of materials employed. It
should be noted that the ISG's used will generally be
controlled as to temperature as well to ensure that
throughout the process the rheologies of the various
materials remain properly matched without degradation
30 having occurred with respect to one or more of the
constituent materials of the melt stream.

This degradation will be a function of the
temperatures experienced within the process as well as
of the time in which the materials are exposed to these

temperatures. Thus, the number of ISG's of a given length which can be employed may be limited, or the length of a given number of ISG's limited. We have found for the ISG's shown in Figures 2 and 3 that longer ISG's result in a more gradual manipulation of the incoming layered melt stream and a greater uniformity of the outgoing stream through the thickness of the stream. This greater uniformity through the thickness of the stream is desirable in lessening the likelihood of unacceptable layer distortions and discontinuities in the finished article. It would therefore be desirable to use longer ISG's in the creation of the composite stream to be formed into the desired configuration, unless degradation of one or more of the materials in the melt stream is a problem. Other considerations may limit the length of the ISG's used for a given resin system and application, such as space limitations, for example, but degradation is of particular concern for most such systems and applications.

The foregoing illustrates one possible approach to applying the processes and apparatus of the present invention, although other approaches are believed possible and should be apparent to persons of ordinary skill in the art in view of the discussion above and of the examples which follow.

It may be that the only properties which are sought to be enhanced by a lamellar construction of an article are those relating to the appearance of the article. The teachings of this disclosure and specifically the apparatus taught herein may be adapted to this

The processes of the present invention and
apparatus for performing the processes, and the articles
which result therefrom are perhaps best further
illustrated by the following examples.

5   Example 1

In this example, a melt stream having a total
of 129 alternating layers of brown and white pigmented
polypropylene was created by extruding the brown and
10   white polypropylene material through a three layer
coextrusion feedblock apparatus, then feeding the
resulting first composite stream through three of the
four-channel Ross static mixers in series.

15   Extrusion rates within the apparatus of the
present invention are in general calculated from the
desired composition ratio in the molded part.
Volumetric screw feeders were used in this and
subsequent examples to meter pellets of the second and
20   of the third compatibilizing material, if present, into
1 1/4 inch single screw 24:1 L:D extruders, with the
extruder screw speeds set to maintain a starve-feed
condition. The screw speed of the 1 3/4 inch single
25   screw 24:1 L:D extruder used for the first material was
then adjusted in this and other examples to obtain the
desired total rate, which is determined by weight
measurements with all of the extruders running.

30   A selection of polymer grades and an adjustment
of individual melt temperatures to ensure a viscosity
mismatch of a factor of no greater than 5 was undertaken
in some of the other examples to obtain an acceptably
uniform distribution of layers in the melt stream cross-
section, as a severe mismatch in polymer viscosities can

cause higher viscosity materials to channel through the
center of the melt stream, resulting in edge-to-edge
layer non-uniformity and local cross-sectional variation
of composition ratio. Because the brown and white
polypropylene used in this example had identical

5   rheologies, however, these adjustments were not required
for this particular example.

Ten ounce cans were transfer molded in a
molding machine from a melt stream constructed as

10 described above, with some cans being made after having
had the melt stream pass through a symmetricizer as
previously described. A layered "gob" was hand cut from
the melt stream emerging from an ISG or from a

15 symmetricizer and was manually deposited into the cold
can mold shown in Figures 10A-C. Cans produced by the
apparatus by bringing piston X and mold core Y together
in the manner suggested by Figures 10A-C were studied by
optical microscopy of specimens cut parallel and

20 perpendicular to the flow direction of the material
being molded, to verify the retention of the lamellar
morphology of the melt stream and to ascertain the
continuity or lack of continuity of the lamellae in the
articles.

25

Substantially continuous layers were observed
in all portions of the cans, and insofar as could be
discerned by optical microscopy, cans formed after the
addition of other ISG's to the series also possessed

30 substantially continuous lamellae.

Fountain flow during mold fill was seen to have

to the mold wall, so that the number of layers in a

cross-section was apparently increased and the
orientation of layers relative to the inner or outer
surfaces of the can varied along the sidewall's length.
The apparent thickness of some of the layers shown in
the accompanying photomicrographs may be somewhat
5   deceiving, then, in that some of the layers must have
been cut on a diagonal. This stretching and folding
over did not appreciably affect the continuity of layers
within the article, though.

10   Considering the photomicrographs of Fig. 7A and
7B, representative can sidewall cross-sections are shown
which demonstrate the effect of the use of a symmetri-
cizer. Layer edges without the symmetricizer solidified
15   to a depth of approximately 20 percent of the wall
thickness from both surfaces before the layers became
substantially parallel to the surfaces.

           In contrast, cans molded from a melt stream
20   proceeding from a symmetricizer exhibited fewer layer
edges at the inner and outer surfaces and layers were
essentially substantially parallel to mold surfaces
throughout the sidewalls of the container, as seen in
Fig. 7A and 7B.

25   It should be noted for future examples using
the can mold and transfer molding apparatus described
above and shown in Fig. 10A-C that some difficulties
were experienced with regard to the bottoms of cans
30   produced by the apparatus. Layer patterns were
generated in the can bottoms which were not matched by
patterns created in the sidewalls of the cans, and such
patterns are believed to be due to a number of factors
peculiar to this transfer molding apparatus and process.

When the "gob" is first dropped into the mold
cavity some solidification occurs, freezing relatively
thick layers at the surface. With the mold closed and
the piston forcing the charge into the can's sidewalls,
5   solidification continues at the piston face and on the
mold core while the molten core materials fill the
sidewalls. With dissimilar polymers, delamination can
occur, and is observed to occur as the bottom is
compressed in the last stage of molding, when much of
10 the material comprising the bottom has already
solidified. Injection molding through a gated mold
cavity will substantially avoid these distortions.

Thus, while transfer molding has initially been
15 used to simulate as nearly as possible actual simple
injection molding in the absence of a suitable injection
molding machine, the difficulties experienced with the
can bottoms just described makes these transfer molded
cans as a whole somewhat inferior with respect to cans
20 which could be expected from actual injection molding,
while such cans as were made are nevertheless sufficient
to demonstrate the operability of the present invention.
To obtain a better representation or approximation of
the multilayer articles which would be produced by such
25 actual injection molding, property evaluation with
respect to the cans of this and other examples has been
limited to the sidewalls thereof whenever possible.

Example 2
30

In this example, the same brown and white
polypropylene was used with a coextrusion feedblock

which were cut from throughout the sidewalls of the
resulting cans, both parallel and perpendicular to the
flow direction of the material being molded, showed
substantially co-continuous lamellae also. Representa-
tive photomicrographs are provided in Figure 11A and
5   11B, and show the lamellae for a given specimen in the
direction of flow and in a direction perpendicular to
the flow of materials during mold-fill.

Example 3

10
In this example, the same apparatus was
employed as in Example 1, except that the can mold of
Figure 10A-C was replaced by the multicavity test
specimen tooling of Fig. 8, and that the three Ross
15   ISG's of Example 1 were replaced by six ISG's of the
variety shown in Fig. 3. The four cavity test specimen
mold was selected to provide standard ASTM test
specimens for purposes of testing mechanical properties
and to more closely simulate conventional injection
20   molding, since in the test specimen mold a lamellar melt
stream would flow through standard runners and gates and
to four mold cavities of differing geometries.

The same brown and white polypropylene
25   materials used in Example 1 were formed into a 129 layer
melt stream, and the melt stream molded into the four
test parts. Optical microscopy of cross-sections taken
in the places indicated in Fig. 8 resulted in the
30   photomicrographs shown in Fig. 9A-H. Substantially
continuous lamellae were observed throughout, and a
substantially uniform composition appeared to have
prevailed throughout all cavities irrespective of runner
length and cavity flow length.

Example 4

This example explores the effects of using an
ISG of the type shown in Fig. 3 versus a commercially
available ISG in an otherwise identical process. Cans
5   were made from the brown and white pigmented poly-
propylene materials of Example 1 in an apparatus
constructed as in Example 1 and using in some runs three
of the Ross ISG's and in other runs six of the ISG's
shown in Fig. 3. Photomicrographs shown in Fig. 4A-F
10 demonstrate clearly that the ISG's of Fig. 3 produce a
significantly better uniformity of layer distribution
than do the Ross ISG's, as has been previously
suggested.

15 Example 5

Multilayer cans were molded from a second
composite stream in two wall thicknesses, 32 and 42
mils, and in the can molding apparatus of Fig. 10A-C. A
20 high density polyethylene was used as the first material
and possessed a melt index of 8 grams per 10 minutes and
a density at 25°C of 0.954 grams per cubic centimeter.
The second material comprised an ethylene vinyl alcohol
copolymer having a 29 mole percent ethylene content, a
25 melt flow rate of 8 grams per 10 minutes, and a density
of 1.21 grams per cubic centimeter at 25°C, such a
copolymer being commercially available under the mark
Soarnol D™ from Nippon Gohsei.

30
Because the HDPE and EVOH do not adhere to one
another well, an anhydride-modified, linear low density
polyethylene-based Plexar 2581™ adhesive resin produced

material for adhering layers of the EVOH and HDPE
together.

Each of the components was fed to an extruder
as in Example 1, and combined in a five layer feedblock
5   in an ABCBA-type layer order having layers of high
density polyethylene, adhesive resin or compatibilizing
material, and EVOH as the A, B, and C, respectively.
The first composite stream thus created was manipulated
in a series of ISG's to form a second composite stream,
10   with both Ross ISG's and those of the type shown in
Fig. 3, respectively, being employed in various runs.
The second composite stream was then passed through a
symmetricizer as in Fig. 5A-C and molded in the
apparatus of Figures 10A-C by dropping a "gob" on the
15   retracted piston X (Fig. 10A), lowering mold core Y
(Fig. 10B), and then raising piston X to simulate
injection molding (Fig. 10C).

The cans of 32 and 42 mil sidewall thicknesses
20   thus formed were subjected to a number of tests, and the
number and type of ISG's used, and the amounts of EVOH
and compatibilizing material used were varied in
different runs to quantify the effect of these
25   variations on the performance characteristics of the
cans.

The following basic measurements were
undertaken:
30

A. <u>Oxygen Barrier Measurements</u> - The molded
cans were double seamed with aluminum lids and sealed
with epoxy. Oxygen permeabilities were measured at 23°C
and 60 percent relative humidity on Modern Control's

Oxtran 1050™ permeability tester. An average of three
cans was tested for each condition or each run.

B. Xylene Permeability Measurements - The cans
were filled with xylene, double seamed with aluminum
5   lids and sealed with an epoxy resin. These were then
placed inside a catch tray in an adequately vented hood,
and weighed as a function of time at regular intervals
over a period of 20 days to monitor the rate of loss of
xylene at ambient temperature. An average of two cans
10 was tested for each condition.

C. Microscopic Verification of Lamellar
Morphology - For verification of the lamellar morphology
in the can walls similar to that undertaken in previous
15 examples, low voltage SEM microscopy was used. Sidewall
cross-sections of the can near the bottom, in the middle
and near the lip were examined in both the axial and
hoop directions.

20   D. Environmental Stress Crack Resistance - To
assess their resistance to environmentally induced
failures, the molded barrier containers associated with
each run were evaluated according to ASTM D2561-84. The
molded cans were filled with 10 percent Igepal® CO630
25 detergent solution produced by GAF Corporation and
double seamed with aluminum lids. Each container was
placed in a separate reclosable plastic storage bag and
placed in the hood at room temperature. The containers
30 were inspected at regular intervals of time for evidence
of cracks or leakage of the contents thereof, with the
time to observation of the failure of a container being

Results of Testing and Discussion of Results

A. Oxygen Barrier Characteristics

The barrier performance of the molded containers was investigated as a function of the total number of layers in the melt stream entering the formation or molding process, the amount of EVOH barrier resin, and the amount of compatibilizing material used.

Before proceeding further it should be noted as discussed in Example 1, that the can molding apparatus depicted in Fig. 10 produced flawed can bottoms which would interfere or which could interfere with the oxygen permeability measurements. Accordingly, to compensate for the flawed bottoms of the containers the oxygen permeability of the whole container was determined first as to each individual container. After a steady state was reached, the bottoms were epoxied and a new steady state transmission rate was recorded. This was undertaken to illustrate the effects of the flawed bottoms on the oxygen transmission data for these lamellar transfer molded containers.

a. The Effect of the Number of Layers in the Stream to be Molded into a Desired Configuration

In order to evaluate the effect of barrier layer thickness on the oxygen transmission rate of the containers as a whole, the number of barrier layers and the total number of layers in the second composite stream was varied over a broad range by adding or removing ISG's of the type shown in Figure 3 and Ross ISG's.

Table 1 summarizes the results of varying
barrier layer thickness on the oxygen permeability of
the 32 mil thick sidewall containers. The data indicate
a minimum in oxygen permeability when the number of
layers in the second composite stream are within the

5   range of 50 to 300. With relatively few layers in the
stream, i.e., less than 50, the thicker barrier layers
do not extend sufficiently in the mold cavity during the
mold fill step to obtain adequate coverage along the
entire length or cross-section of a container wall.

10   With a large number of layers, the barrier layers are
too thin and tend to become discontinuous. This has
been confirmed by photomicrographs corresponding to
having 1025 layers in the second composite stream, as

15   compared to cross-sectional photomicrographs of articles
molded from a second composite stream having 257 total
layers. The tendency of the layers to become
discontinuous causes the barrier performance of the
container as a whole to eventually approach that of a

20   conventional melt blend.

25

30

Table 1. Effect of Number of Layers in Stream to Be
          Molded on Oxygen Transmission Rate of 32
          Mil Wall Containers

Number of Barrier Layers	Total Number of Layers	Oxygen Transmission Rate (cc/day atm. pkg)	
		Whole Container	Bottom Epoxied
8	33	0.0075	0.0066
16	65	0.0106	0.0050
32	129	0.0068	0.0038
64	257	0.0059	0.0046
128	513	0.0166	0.0078
256	1025	0.0256	0.0238
512	2049	0.0443	0.0386
Melt Blend	---	0.5280	---
HDPE Control	---	0.3651	0.3060

        The minimum in oxygen permeability in the 50
to 300 total layers range in the second composite stream
amounts to approximately an 80-fold improvement in
barrier performance as compared to an identically
composed melt blend. The barrier level achieved in the
containers of this example is equivalent to an oxygen
ingression rate of less than 1.4 cubic centimeters in 12
months.

        The oxygen permeability results as a
function of the number of layers in the second composite
stream for 42 mil thick sidewall containers are
summarized in Table 2. The results indicate essentially
the same trend in the dependence of the oxygen

transmission rate of the cans on the number of layers in
the second composite stream. In the 42 mil thick
sidewall containers, below about 800 layers in the
second composite stream, the barrier performance of the
lamellar injection molded containers approaches that of
5   a coextruded sheet with a perfectly uniform and
continuous barrier layer in the structure.

10   Table 2.   Effect of Number of Layers in the Stream to
be Molded on Barrier Performance of 42 mil
Wall Containers, HDPE/Plexar 2581 /Soarnol D

Number of Barrier Layers	Total Number of Layers	Oxygen Transmission Rate (cc/day . atm . pkg)	
		Whole Container	Bottom Epoxied
16	65	0.0003	0.0003
64	257	0.0007	0.0004
256	1025	0.0012	---
1024	4097	0.0163	0.0096
16384	65537	0.0640	0.0508
Melt Blend	---	0.2755	0.2455

The barrier level of about 0.001 cubic
centimeters per day per atmosphere per package achieved
with these containers, which is the lowest barrier level
30   which can be reliably reported given the measurement
techniques used, is equivalent to an oxygen ingression
rate of less than 1 cubic centimeter in a two year time

b.   The Effect of the Amount of EVOH Barrier
Material in the Structure

         Table 3 summarizes the oxygen permeability
data for lamellar molded 42 mil thick sidewall cans with
a varying amount of the EVOH barrier material
incorporated within the containers. The total number of
layers in the second composite stream which was molded
was kept the same in each case at a total of 257 layers.
The results indicate that at least 10 percent by weight
of the particular EVOH material used is the minimum
amount required to achieve the barrier levels of 0.001
cubic centimeters per day per atmosphere per package
which were noted in Table 2.

Table 3.   Effect of Amount of EVOH in Structure in
           Performance of 42 Mil Wall Containers, 257
           layers total HDPE/Plexar 2581/Soarnol D

Amount of Soarnol D, wt. %	Oxygen Transmission Rate (cc/day . atm . pkg)	
	Whole Container	Bottom Epoxied
5	0.0062	---
10	0.0008	0.0005
15	0.0003	---

c.   The Effect of the Amount of Plexar 2581™
Compatibilizing Material

         Oxygen permeability measurements on con-
tainers having 257 total layers in the second composite
stream and with 15 percent or 25 percent by weight of
the Plexar 2581™ compatibilizing material showed no

-38-

significant difference between the containers so
constructed.

Given that a significant use of barrier resins
is in food packaging and packaging materials, and given
5   also that many consumers may prefer a pigmented or
opaque packaging material, the effect on oxygen barrier
performance of the addition of titanium dioxide pigment
to 32 and 42 mil cans having 257 total layers was
studied. The results show that the oxygen permeability
10 characteristics of the 42 mil cans was not significantly
affected by the addition of titanium dioxide while the
32 mil cans exhibited a noticeable loss of barrier due
to larger titanium dioxide particles bursting through
15 the thin layers of EVOH.

B. Xylene Permeation Characteristics

Many of the factors which were tested with
regard to the oxygen permeability of cans molded from
20 the high density polyethylene/Plexar/Soarnol D system
were considered with regard to xylene permeation
characteristics also, with the effect of the total
number of layers on the xylene permeability of 32 mil
can containers being summarized in Table 4. The data
25 indicate a minimum in xylene permeability in the range
of from about 50 to about 300 total layers in the second
composite stream, which is similar to what was noted in
the case of oxygen permeability. This minimum amounts
30 to approximately a 160-fold improvement in barrier
performance to xylene compared with a 32 mil high
density polyethylene can. The melt blend apparently

achieved in the 32 mil cans is equivalent to a xylene

weight loss of less than .01 percent in 12 months. By
comparison, there was virtually no loss of xylene to the
atmosphere in a 20 day period from a 42 mil high density
polyethylene/Soarnol D™ can.

5

Table 4.   Effect of Number of Layers in Stream to be
            Molded on Xylene Permeation Rate of
            HDPE/Soarnol D 32 Mil Wall Containers

No. of Barrier Layers	Total No. of Layers	Wt Loss of Xylene mg/hr
8	33	0.657
16	65	0.371
32	129	0.201
64	257	0.363
128	513	0.461
256	1025	1.811
512	2049	2.791
Melt Blend	---	36.571
HDPE Control	---	32.600

        The addition of titanium dioxide pigment had a
negligible effect on xylene permeability in this system
for 42 mil thick cans molded from a second composite
stream having 257 total layers.

                C. Environmental Stress Crack Resistance

        The cans which were tested showed no evidence
of failure even after 240 hours at room temperature.
Typically an acceptable environmental stress crack
resistance for cans made from polyethylene, for example,
is 120 hours.

Example 6

        In this example multilayer cans were molded as
in Example 5, but with a resin system including high
density polyethylene having a melt index of 0.7 grams
5   per 10 minutes and a density of 0.96 grams per cubic
centimeter as the first material, Selar® PA3426
amorphous nylon having a reported density of 1.19 grams
per cubic centimeter (commercially available from E. I.
du Pont De Nemours and Company Inc. Wilmington,
10 Delaware) as the second material, and the assignee's
Primacor® 1410 coextrudable tie layer resin, having a
melt index of 1.5 grams per 10 minutes and a density of
0.938 grams per cubic centimeter, as the third material.

15   The cans which resulted were subjected to
xylene and oxygen barrier tests which are described in
detail in Example 5. The xylene permeability results
are summarized in Table 5, and show that the high
density polyethylene/nylon/Primacor® 42 mil molded
20 containers exhibit over a fifty-fold improvement in
xylene permeability over a 42 mil high density
polyethylene can at ambient temperatures. This
improvement appears to be comparable with the
25 permeability figures reported in United States Patent
Nos. 4,410,482 to Subramanian, 4,416,942 to DiLuccio,
and 4,444,817 to Subramanian for articles made by an
extrusion blow molding process.

30

Table 5.   Xylene Permeability of HDPE/Amorphous
            Nylon Containers

Structure	Avg. Weight Loss of Xylene	
	mg/hr	%/hr
HDPE	32.031	0.0109
HDPE (71% by volume)/Primacor 1410 (13%)/Selar PA 3426 (16%)	0.607	0.0007

*256 barrier layers (1025 total layers)

        The oxygen permeability characteristics of the
42 mil thick molded cans of this example are shown in
Table 6. An eight-fold improvement in oxygen barrier
performance over cans molded from high density
polyethylene alone is evident. This figure is also
similar to the improvement in oxygen barrier achieved
with a high density polyethylene/Selar® RB nylon laminar
mixing process, as reported in Subramanian,
"Permeability Barriers by Controlled Morphology of
Polymer Blends," Polymer Engineering Science, Volume 25,
No. 8, Mid June 1985.

Table 6.   Oxygen Barrier Performance of
           HDPE/Amorphous Nylon Containers

Structure	Oxygen Transmission Rate (cc/day. atm. package)	
	Whole Container	Bottom Epoxied
HDPE	---	0.1980
HDPE (71% by volume)/Primacor 1410 (13%)/Selar PA 3426 (16%)	0.356	0.0254

*256 barrier layers (1025 total layers)

Example 7

     This example used the apparatus and process of
Examples 1 and 2 in exploring a system having poly-
propylene as the structural component, rather than the
HDPE previously studied, with the same EVOH as used in
previous examples. Cans were molded in the 32 mil and
42 mil wall thicknesses according to the procedures set
forth in Example 1, and the barriers of these containers
to oxygen and xylene were studied as a function of
several variables.

     With regard to oxygen barrier, the effects of
the amount of EVOH barrier resin in the structure, and
of the particular compatibilizing material used were
studied.

     a.   Effect of Amount of EVOH Barrier Resin

by a melt flow index of 12 and a density of 0.903 grams
per cubic centimeter as a first material, Soarnol D®
EVOH as a second material, and Admer QF-500 tie layer
resin from Mitsui Petrochemicals Industries, Ltd. (an
anhydride-grafted polypropylene with a melt flow rate
5 (MFR) of 3 grams per 10 minutes and a density of 0.91
grams per cubic centimeter) as the third material at 25
percent by weight throughout.

       The results of oxygen permeability testing
10 conducted as in previous examples for the effect of
various amounts of the EVOH barrier resin are shown in
Table 7, and correspond to a barrier efficiency of about
50% relative to an ideally coextruded 1025 layer
coextruded sheet. The lower barriers achieved were
15 believed indicative of substantial layer break-up and
discontinuities in the molded can walls. Scanning
electron microscopy of sidewall cross-sections near the
bottom, middle and top of the can in both the axial and
20 hoop directions confirmed that such layer breakup was
present.

25

30

Table 7.   Effect of Amount of EVOH in Structure
           on Barrier Performance of PP/EVOH
           Containers

Amount of EVOH, Wt Percent	Oxygen Transmission Rate (cc/day. atm. package)	
	Whole Container	Bottom Epoxied
10	0.0117	0.0100
15	0.0067	0.0022
20	---	0.0025

*256 barrier layers (1025 total layers)
PP and 25 wt % Admer QF500 tie layer resin

b.   Effect Of Compatibilizing Material

Though the Admer QF-500® tie layer resin
exhibited strong interfacial adhesion in preliminary
testing with the EVOH and polypropylene materials
selected, with peel strengths in five-layer coextruded
sheets of 5.2 pounds per inch and 7.5 pounds per inch in
the machine and transfer directions, respectively, at
the 5 percent level by weight, the molded cans
delaminated easily with a gentle squeeze or in some
cases only with the air ejection of the cans from the
mold.

In an attempt to explore ways to improve the
adhesion between the polypropylene and EVOH layers,
other compatibilizing materials were evaluated.   These
were Admer QF-551 tie layer material from Mitsui (an
anhydride-grafted polypropylene with an MFR of 5.7 and a

functionalized triblock SEBS copolymer of a density of

0.91 grams per cubic centimeter). A comparison of
oxygen permeation data for cans molded using the
original Admer® QF-500 and the Kraton® FG-1901X
materials shows the Admer® QF-500 tie layer material to
be superior (see Table 8). In a comparison between the
Admer® QF-500 and Admer® QF-551 tie layer resins, the
latter resulted in better looking cans but no
significant improvement in barrier or adhesion was
observed.

It was also thought that increasing the melt
temperature of the charged composite stream might
increase the flow of the Admer® QF-500 compatibilizing
material and improve adhesion. Increasing the
temperature of the charged composite stream from 440°F-
475°F showed no improvement in adhesion or barrier
performance, however.

Table 8. Effect of Compatibilizing Material in
          Structure on Barrier Performance of 42
          Mil PP/EVOH Containers

Compatibilizing Material	Oxygen Transmission Rate (cc/day. atm. package)	
	Whole Container	Bottom Epoxied
Admer™ QF500	0.0021	0.0017
Kraton™ G1901X	0.0351	0.0272

*64 barrier layers (257 total layers)
65% PP and 10 wt % Soarnol™ D EVOH

Some testing was also done of the containers
and of the various materials and amounts thereof for
xylene permeation resistance. The use of 10 percent
Soarnol D® EVOH resulted in a one hundred seventy-two-
fold improvement in xylene permeation resistance over a
polypropylene control. An additional 5 percent by
weight of the Soarnol D® EVOH brought the improvement to
nearly a thousand-fold. (See Table 9)

Table 9. Effect of Amount of EVOH in Structure on
          Xylene Permeation of PP/EVOH Containers

Amount of SOARNOL™ D EVOH (wt %)	Avg. Wt. Loss of Xylene mg/hr
0	122.37
10	0.709
15	0.127
20	0.027

*64 barrier layers (257 total layers)
PP and 25 wt % Admer™ QF500 compatibilizing
material

Where the barrier resin used was Eval® F resin
(1.3 melt index, 1.19 grams per cubic centimeter
density,Kuraray Company, Ltd.), the xylene permeation
rate through 32 mil thick wall containers molded from a
257 layer composite stream corresponded to 1.287
milligrams per hour of xylene weight loss. This figure

one hundred seventy-two-fold improvement with 10 percent
Soarnol D® EVOH.

Example 8

5   In this example and in Examples 9 and 10, the
effects of a lamellar construction are explored in terms
of the environmental stress crack resistance(ESCR),
deflection temperature under load(DTUL), and heat sag of
various structural systems. In this and subsequent
10 examples where performed, the environmental stress crack
resistance for a test specimen was determined according
to ASTM D1693 with synthetic gasoline (75 weight percent
isooctane and 25 weight percent toluene) at 2000 psi
constant applied stress. The distortion temperature
15 under load for unannealed and annealed specimens was
determined according to ASTM D648, and the heat sag
after a specimen had been exposed to a temperature of
250 degrees Fahrenheit for a period of an hour.

20   This example looks primarily at systems of
polycarbonate/polybutylene terephthalate (PBT) which are
comprised of 15 parts and 30 parts of Celanex® 2002 PBT
from Hoechst Celanese with the remaining 85 and 70
parts, respectively, comprising the assignee's Calibre®
25 300-10 polycarbonate. The Celanex™ 2002 material
possessed a reported density of 1.31 grams per cubic
centimeter (with no melt index provided by the
manufacturer), while the assignee's polycarbonate
30 material had a melt index of 10 grams per 10 minutes and
a density of 1.2 grams per cubic centimeter.

Test specimens were for one set of tests molded
using the same equipment, except for the substitution of
a four cavity test specimen mold as detailed earlier,

and according to the same general procedures used in
previous Examples from layered composite streams having
33, 65, 129, 257, 513 and 1,025 total layers, and from a
melt blend both by transfer and injection molding. Test
results from the first set of tests for the basic 85/15
5 system are reported in Table 10, while the results for
the basic 70/30 system are shown in Table 11. The
results obtained for a polycarbonate/toughened PBT
system are provided in Table 12. Based on additional
tests conducted to determine the effect of a lamellar
10 construction on other structural properties, no loss in
other structural properties was seen for any of the
specimens thus made and otherwise tested compared to
specimens formed from a melt blend of the same
15 materials.

Table 10. Lamellar Molded PC/PBT (85/15) Specimens
                Effect of Number of Layers in Stream to be Molded

No. of Layers	ESCR(min.)	DTUL Unannealed/Annealed (°C/°C)		Heat Sag (mm)
		@ 66 psi	@ 264 psi	
33	94.3±42.9	140.4/151.6	118.1/149.4	1.8±1.4
65	81.3±12.3	140.5/150.1	125.0/147.6	3.4±0.3
129	51.0±4.6	137.8/148.0	120.2/146.0	2.5±0.3
257	68.3±8.1	135.3/150.6	121.8/146.4	2.5±1.1
513	64.0±10.5	135.6/146.5	116.6/142.0	2.7±1.1
1025	52.0±4.6	133.0/145.7	116.5/140.8	3.2±1.3
Melt Blend, Injection Molded	15.0±0.1			
Melt Blend, Transfer Molded	14.7±2.1	116.5/125	104.9/120.0	34.7±

25

30

Table 11. Lamellar Molded PC/PBT (70/30) Specimens
Effect of Number of Layers in Stream to be Molded

No. of Layers	ESCR(min.)	DTUL Unannealed/Annealed (°C/°C)		Heat Sag(mm)
		@ 66psi	@ 264psi	
33	203.7±22.5	139.1/151.6	119.2/149.3	3.4±0.7
65	193.5±20.5	138.7/149.5	118.2/147.0	5.5±0.9
129	167.7±36.2	136.8/147.6	116.0/143.7	3.9±0.3
257	198.7±22.0	133.7/150.2	109.5/145.3	3.8±1.7
513	210.3±101	133.4/146.1	120.2/141.8	2.8±1.0
1025	153.5±27.6	133.2/144.7	111.6/139.5	3.5±0.4
Melt Blend, Transfer Molded	176.0±58.0	116.9/125.4	101.2/120.2	33.1±0.1

20 Table 12. Lamellar Molded PC/PBT (85/15) (Toughened)
Specimens. Effect of Number of Layers in
Stream to be Molded

No. of Layers	DTUL Unannealed/Annealed (°C/°C)	
	@ 66 psi	@ 264 psi
65	135.4/148.2	116.0/144.8
257	133.0/147.3	120.0/143.2
Melt Blend, Transfer Molded	116.0/123.3	106.8/118.4
30 Melt Blend, Injection Molded	114.9/122.4	103.7/117.8

25

equipment and having the same number of layers as a
three different proportions of the materials to examine

the effect of composition changes on the DTUL and ESCR
of the specimens. The results from these tests are
reported in Table 13, and again, no loss in other
structural properties was seen for specimens made and
tested as indicated.

5

Table 13. Effect of Composition (129 layers)

Amount of PBT (wt %)	ESCR(min.)	DTUL Unannealed/Annealed (°C/°C)		Heat Sag(mm)
		@ 66 psi	@ 264 psi	
15	51.0±4.6	137.8/148.0	120.2/146.0	2.5±0.3
30	167.7±36.2	136.8/147.6	116.0/143.7	3.9±0.3
50	>5700	133.9/146.6	102.0/140.4	--

Example 9

20

This example looks at the benefits accruing
from a lamellar construction in terms of the
environmental stress crack resistance and deflection
temperature under load of systems having 15 and 30 parts
of Celanex® 2002 PBT by weight and 85 and 70 parts,
25 respectively, of a 65 to 35 part polycarbonate/ABS
blend, as a function of the total number of layers
formed in the composite stream to be molded. The blend
had a melt index of 3 grams per 10 minutes (230°C/3.8
kg) and a density of 1.12 grams per cubic centimeter,
30 while the PBT had the properties ascribed to the Hoechst
Celanese material previously. Test members were molded
as in Example 8, with the same maintenance of other
physical or structural properties seen in Example 8.
The ESCR and DTUL results are reported in Tables 14 and
15 below, respectively, for the 85/15 and 70/30 systems.

Table 14. Effect of Number of Layers in Stream to be Molded
            - PC/ABS Blend/PBT (85/15)

No. of Layers	ESCR(min.)	DTUL Unannealed/Annealed (°C/°C)		Heat Sag (mm)
		@ 66 psi	@ 264 psi	
33	56.7±25.0	123.6/137.5	93.8/127.9	11.6±0.7
65	86.3±32.5	124.1/128.0	99.8/115.2	10.0±1.1
129	58.7±12.7	125.0/137.5	96.2/132.3	10.3±
257	30.7±8.3	122.8/135.9	95.3/124.3	21.9±1.5
513	53.7±6.4	120.2/132.5	92.9/122.2	16.7±2.1
1025	34.0±4.4	118.1/130.9	89.0/120.7	23.9±1.0
Melt Blend, Transfer Molded	8.7±0.6	96.1/105.6	86.6/102.1	125.6±
Melt Blend, Injection Molded	12.0±3.0	95/106	86/99	-

Table 15. Effect of Number of Layers in Stream to be Molded
            - PC/ABS Blend/PBT (70/30)

No. of Layers	ESCR(min.)	DTUL Unannealed/Annealed (°C/°C)		Heat Sag (mm)
		@ 66 psi	@ 264 psi	
33	95.7±24.0	123.3/137.6	96.1/130.1	8.3±2.7
65	121.7±23.4	124.7/137.3	97.1/129.2	7.8±4.7
129	107.0±8.7	123.9/136.4	98.3/128.6	11.0±3.0
257	93.0±31.0	119.1/131.9	92.2/120.0	15.2±3.2
513	117.3±22.8	118.1/131.2	87.3/122.4	12.6±1.3
1025	100.0±14.9	113.3/128.4	86.0/115.7	16.4±2.0
Melt Blend, Transfer Molded	64.0±10.5	92.8/103.4	75.6/97.4	80.1±1.4
Melt Blend,	12.7±1.2	89/101	73/92	

Example 10

This example explores the environmental stress
crack resistance and deflection temperature under load
of test articles molded from composite streams having
various numbers of layers of the assignee's Calibre®
300-10 polycarbonate (melt index of 10 grams per 10
minutes;density of 1.2 grams per cubic centimeter) and
Traytuf® 1006-C polyethylene terephthalate (PET) from
The Goodyear Tire and Rubber Company (melt index not
reported; density of 1.37 grams per cubic centimeter),
in systems comprising 30 parts PET with 70 parts
polycarbonate by weight, and 15 parts PET with 85 parts
polycarbonate by weight. The molding and testing
procedures and equipment were those used in Examples 8
and 9 above. Test results are reported in Tables 16 and
17, and again no loss of other structural properties was
observed compared to a melt blend of the materials in
these systems.

Table 16. Effect of Number of Layers in Stream to be Molded
          - PC/PET (85/15)

No. of Layers	ESCR(min.)	DTUL Unannealed/Annealed (°C/°C)		Heat Sag (mm)
		@ 66 psi	@ 264 psi	
65	24.3±5.9	137.5/147.8	111.4/145.5	4.5±0.4
129	24.3±0.6	136.2/148.7	113.2/146.0	3.4±0.6
257	25.0±6.2	134.6/147.6	112.0/145.3	5.3±1.2
513	25.0±5.2	138.0/148.1	108.7/145.8	5.6±0.4
1025	26.0±3.5	137.5/148.2	109.6/145.6	4.8±0.3
Melt Blend, Transfer Molded	11.3±1.5	131.7/144.3	107.4/141.5	4.5±0.3

Table 17. Effect of Number of Layers in Stream to be Molded
          - PC/PET (70/30)

No. of Layers	ESCR(min)	DTUL Unannealed/Annealed (°C/°C)		Heat Sag (mm)
		@ 66 psi	@ 264 psi	
65	23.0±2.0	133.4/147.4	97.8/144.6	6.0±0.4
129	32.3±5.1	135.5/148.5	100.3/145.9	4.2±0.9
257	22.0±1.7	136.2/147.8	97.5/145.5	7.0±1.0
513	34.3±1.5	135.7/148.7	101.4/146.6	5.5±0.4
1025	26.0±1.0	133.3/147.5	100.7/144.2	7.2±0.8
Melt Blend, Transfer Molded	19.3±4.0	125.4/142.6	97.2/139.7	5.8±0.4

15   The foregoing examples demonstrate that the
processes and apparatus of the present invention are
well suited for overcoming the deficiencies of the known
art.

20   Large improvements in barrier to gases and
solvents and in environmental stress crack resistance,
and additional improvements in distortion temperature
under load, are seen to result from such a lamellar
construction compared to articles comprised of a melt
25   blend of the same materials in the same proportions.

        Similar improvements in filled systems with
respect to the control of the coefficient of linear
thermal expansion of an article, in the shielding of
30   electromagnetic interference, and in ignition resistance
should also be available by the lamellar constructions
made possible by the present invention.

WHAT IS CLAIMED IS:

1. A process for making a moldable multilayer plastic article, comprising the steps of:

coextruding discrete, generally planar layers of first and second diverse thermoplastic resinous materials in a first composite stream; and

forming the first composite stream into a desired configuration by some process other than thermoforming.

2. A process as defined in Claim 1, wherein the first composite stream is formed into a desired configuration by injection molding, transfer molding, compression molding, injection blow molding, extrusion blow molding, or displacement blow molding.

3. A process as defined in Claims 1 or 2, wherein the first composite stream is formed into a desired configuration having at least one critical surface such that a plurality of layers of the first and second materials lie generally parallel to such surface.

4. A process as defined in Claims 1 or 2, wherein the first composite stream is injected into a

plurality of mold cavities as part of a multicavity
injection molding process.

5. A process for making a moldable multilayer
plastic article, comprising the steps of:

5   coextruding discrete, generally planar layers
of first and second diverse thermoplastic resinous
materials in a first composite stream;

         manipulating the first composite stream to form
10   a second composite stream having an increased number of
discrete, generally planar layers of the first and
second diverse thermoplastic materials compared to the
first composite stream; and

15   forming the second composite stream into a
desired configuration by some process other than
thermoforming.

6. A process as defined in Claim 5, wherein
20   the second composite stream is formed into a desired
configuration by injection molding, transfer molding,
compression molding, injection blow molding, extrusion
blow molding, or displacement blow molding.

25   7. A process as defined in Claims 5 or 6,
wherein the step of manipulating the first composite
stream to form the second composite stream includes:

         dividing the first composite stream to form a
30   plurality of substreams collectively containing an
increased number of discrete, generally planar layers of
the first and second materials compared to the first

stacking the plurality of substreams.

8.   A process as defined in Claim 7, wherein
the dividing and stacking steps are accomplished by
passing the first composite stream through one or more
interfacial surface generators.

9.   A process as defined in Claims 5 or 6,
wherein the second composite stream is formed into a
desired configuration having at least one critical
surface such that a plurality of layers of the first and
second materials lie generally parallel to such surface.

10.   A process as defined in Claims 5 or 6,
wherein the second composite stream is injected into a
plurality of mold cavities as part of a multicavity
injection molding process.

11. A process as defined in Claims 4 or 10,
wherein the mold cavities possess differing geometries.

12. A process as defined in Claims 4, 10 or 11,
wherein at least one of the first and second materials
comprises less than 15 percent by volume of the injected
stream.

13. A process as defined in Claim 12, wherein
layers of the at least one material extend fully
throughout the plurality of mold cavities and the
multilayer articles produced therefrom.

14. A process as defined in Claims 3 or 9,
wherein no more than 10 percent of the layers of the
first and second materials adjacent the critical surface
have an interfacial surface area to unit thickness ratio
of less than 10 to 1.

15. A process as defined in Claims 3 or 9, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface are individually substantially uniformly thick.

16. A process as defined in Claims 3 or 9, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 100 to 1.

17. A process as defined in Claim 16, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 1000 to 1.

18. A process as defined in Claims 3 or 9, wherein the desired configuration possesses a uniformity of composition with respect to at least the first and second materials adjacent the critical surface.

19. A process as defined in Claims 3 or 9, wherein the layers of the first and second materials lying generally parallel to the critical surface are evenly distributed across a cross-section of the article adjacent such surface.

20. A process for making a moldable multilayer plastic article, comprising the steps of:

    coextruding discrete, generally planar layers

stream, the selected layer order being characterized by

the placement of a layer of the third material between
any otherwise adjacent layers of the first and second
materials; and

forming the first composite stream into a
desired configuration by some process other than
thermoforming.

21. A process as defined in Claim 20, wherein
the first composite stream is formed into a desired
configuration by injection molding, transfer molding,
compression molding, injection blow molding, extrusion
blow molding, or displacement blow molding.

22. A process as defined in Claims 20 or 21,
wherein the first composite stream is formed into a
desired configuration having at least one critical
surface such that a plurality of layers of the first,
second and third materials lie generally parallel to
such surface in said selected layer order.

23. A process as defined in Claims 20 or 21,
wherein the first composite stream is injected into a
plurality of mold cavities as part of a multicavity
injection molding process.

24. A process for making a moldable multilayer
plastic article, comprising the steps of:

coextruding discrete, generally planar layers
of first, second and third diverse thermoplastic
resinous materials in a selected layer order in a first
composite stream, the selected layer order being
characterized by the placement of a layer of the third

material between any otherwise adjacent layers of the
first and second materials;

5
manipulating the first composite stream to form
a second composite stream having an increased number of
discrete, generally planar layers of the first and
second diverse thermoplastic materials compared to the
first composite stream; and

10
forming the second composite stream into a
desired configuration by some process other than
thermoforming.

15
25. A process as defined in Claim 24, wherein
the second composite stream is formed into a desired
configuration by injection molding, transfer molding,
compression molding, injection blow molding, extrusion
blow molding, or displacement blow molding.

20
26. A process as defined in Claims 24 or 25,
wherein the step of manipulating the first composite
stream to form the second composite stream includes:

25
dividing the first composite stream to form a
plurality of substreams collectively containing an
increased number of discrete, generally planar layers of
the first, second and third materials compared to the
first composite stream; and

stacking the plurality of substreams.

30
27. A process as defined in Claim 26, wherein
the dividing and stacking steps are accomplished by
passing the first composite stream through one or more

28. A process as defined in Claims 24 or 25, wherein the second composite stream is formed into a desired configuration having at least one critical surface such that a plurality of layers of the first, second and third materials lie generally parallel to such surface in said selected layer order.

29. A process as defined in Claims 24 or 25, wherein the second composite stream is injected into a plurality of mold cavities as part of a multicavity injection molding process.

30. A process as defined in Claims 23 or 29, wherein the mold cavities possess differing geometries.

31. A process as defined in Claims 23, 29 or 30, wherein at least one of the first, second and third materials comprises less than 15 percent by volume of the injected stream.

32. A process as defined in Claim 31, wherein layers of the at least one material extend fully throughout the plurality of mold cavities and the multilayer articles produced therefrom.

33. A process as defined in Claims 22 or 28, wherein no more than 10 percent of the layers of the first, second and third materials adjacent the critical surface have an interfacial surface area to unit thickness ratio of less than 10 to 1.

34. A process as defined in Claims 22 or 28, wherein at least the plurality of layers of the first, second and third materials lying generally parallel to

the critical surface are individually substantially uniformly thick.

35. A process as defined in Claims 22 or 28, wherein at least the plurality of layers of the first, second and third materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 100 to 1.

36. A process as defined in Claim 35, wherein at least the plurality of layers of the first, second and third materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 1000 to 1.

37. A process as defined in Claims 22 or 28, wherein the desired configuration possesses a uniformity of composition with respect to at least the first, second and third materials adjacent the critical surface.

38. A process as defined in Claims 22 or 28, wherein the layers of the first, second and third materials lying generally parallel to the critical surface are evenly distributed across a cross-section of the article adjacent such surface.

39. Apparatus for performing the process of any of Claims 1-38.

40. A multilayer plastic article made by the process of any of Claims 1-38.

41. An asymmetrical moldable multilayer plastic

a plurality of diverse thermoplastic resinous materials
extending continuously throughout the article.

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AMENDED CLAIMS

[received by the International Bureau on 22 May 1991 (22.05.91);
original claims 11,12,14-16,18,19 amended; 30,31,33-35,37,
38,39 and 40 other claims unchanged (4 pages)]

stacking the plurality of substreams.

8.   A process as defined in Claim 7, wherein
the dividing and stacking steps are accomplished by
passing the first composite stream through one or more
interfacial surface generators.

9.   A process as defined in Claims 5 or 6,
wherein the second composite stream is formed into a
desired configuration having at least one critical
surface such that a plurality of layers of the first and
second materials lie generally parallel to such surface.

10.   A process as defined in Claims 5 or 6,
wherein the second composite stream is injected into a
plurality of mold cavities as part of a multicavity
injection molding process.

11. A process as defined in Claim 4, wherein
the mold cavities possess differing geometries.

12. A process as defined in Claim 11, wherein
at least one of the first and second materials comprises
less than 15 percent by volume of the injected stream.

13. A process as defined in Claim 12, wherein
layers of the at least one material extend fully
throughout the plurality of mold cavities and the
multilayer articles produced therefrom.

more than   percent of the layers of the first and
second materials adjacent the critical surface have an
interfacial surface area to unit thickness ratio of less
than 10 to 1.

15. A process as defined in Claim 3, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface are individually substantially uniformly thick.

16. A process as defined in Claim 3, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 100 to 1.

17. A process as defined in Claim 16, wherein at least the plurality of layers of the first and second materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 1000 to 1.

18. A process as defined in Claim 3, wherein the desired configuration possesses a uniformity of composition with respect to at least the first and second materials adjacent the critical surface.

19. A process as defined in Claim 3, wherein the layers of the first and second materials lying generally parallel to the critical surface are evenly distributed across a cross-section of the article adjacent such surface.

20. A process for making a moldable multilayer plastic article, comprising the steps of:

coextruding discrete, generally planar layers of first, second and third diverse thermoplastic materials in a selected layer order in a first composite stream, the selected layer order being characterized by the placement of a layer of the third material between

surface such that a plurality of layers of the first,
second and third materials lie generally parallel to
such surface in said selected layer order.

29.   A process as defined in Claims 24 or 25,
wherein the second composite stream is injected into a
plurality of mold cavities as part of a multicavity
injection molding process.

30. A process as defined in Claim 23, wherein
the mold cavities possess differing geometries.

31. A process as defined in Claim 30, wherein
at least one of the first, second and third materials
comprises less than 15 percent by volume of the injected
stream.

32. A process as defined in Claim 31, wherein
layers of the at least one material extend fully
throughout the plurality of mold cavities and the
multilayer articles produced therefrom.

33. A process as defined in Claim 22, wherein
no more than 10 percent of the layers of the first,
second and third materials adjacent the critical surface
have an interfacial surface area to unit thickness ratio
of less than 10 to 1.

34. A process as defined in Claim 22, wherein
at least the plurality of layers of the first, second
and third materials lying generally parallel to the
critical surface are individually substantially
uniformly thick.

at least the plurality of layers of the first, second

and third materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 100 to 1.

36. A process as defined in Claim 35, wherein at least the plurality of layers of the first, second and third materials lying generally parallel to the critical surface have interfacial surface area to unit thickness ratios of at least 1000 to 1.

37. A process as defined in Claim 22, wherein the desired configuration possesses a uniformity of composition with respect to at least the first, second and third materials adjacent the critical surface.

38. A process as defined in Claim 22, wherein the layers of the first, second and third materials lying generally parallel to the critical surface are evenly distributed across a cross-section of the article adjacent such surface.

39. Apparatus for performing the process of any of Claims 1, 5, 20 or 24.

40. A multilayer plastic article made by the process of any of Claims 1, 15, 20 or 24.

41. An asymmetrical moldable multilayer plastic article comprising at least about 17 discrete layers of a plurality of diverse thermoplastic resinous materials extending continuously throughout the article.
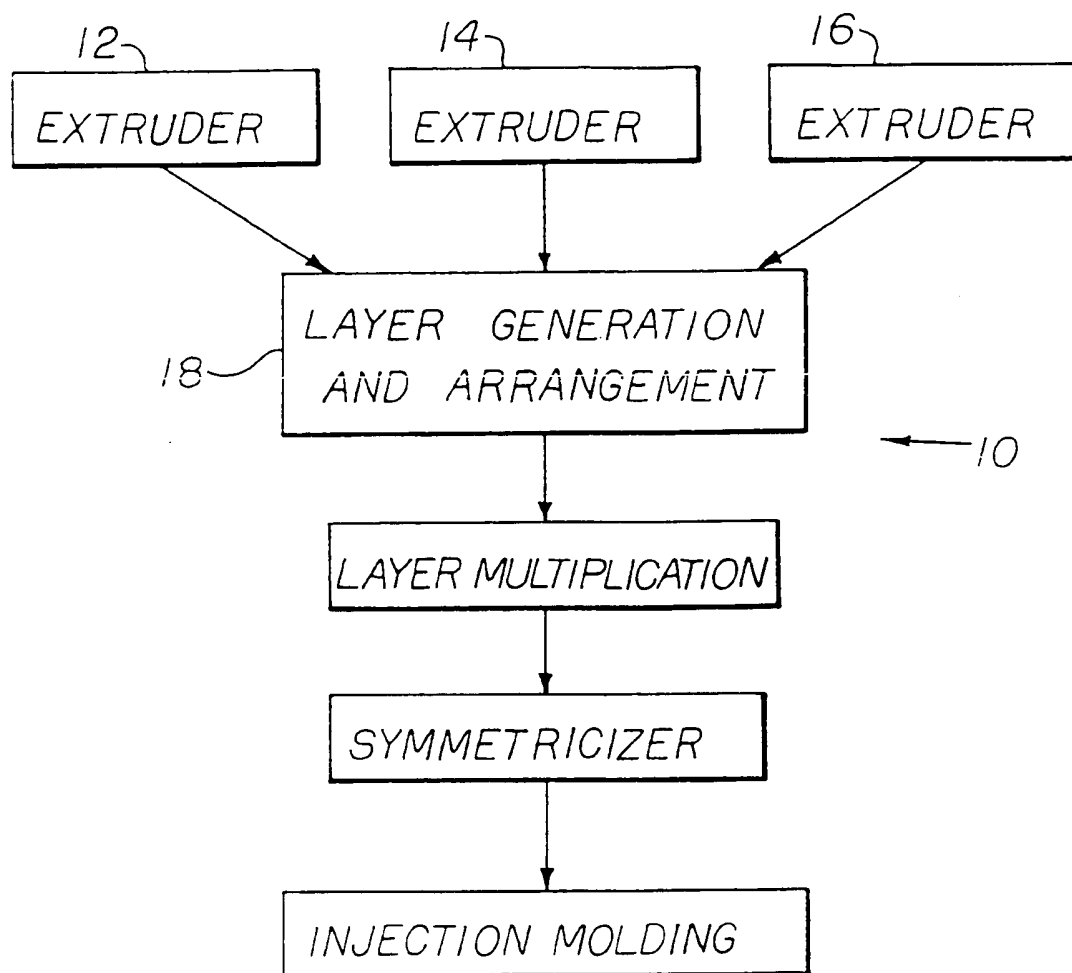
FIG. I

FIG. 2
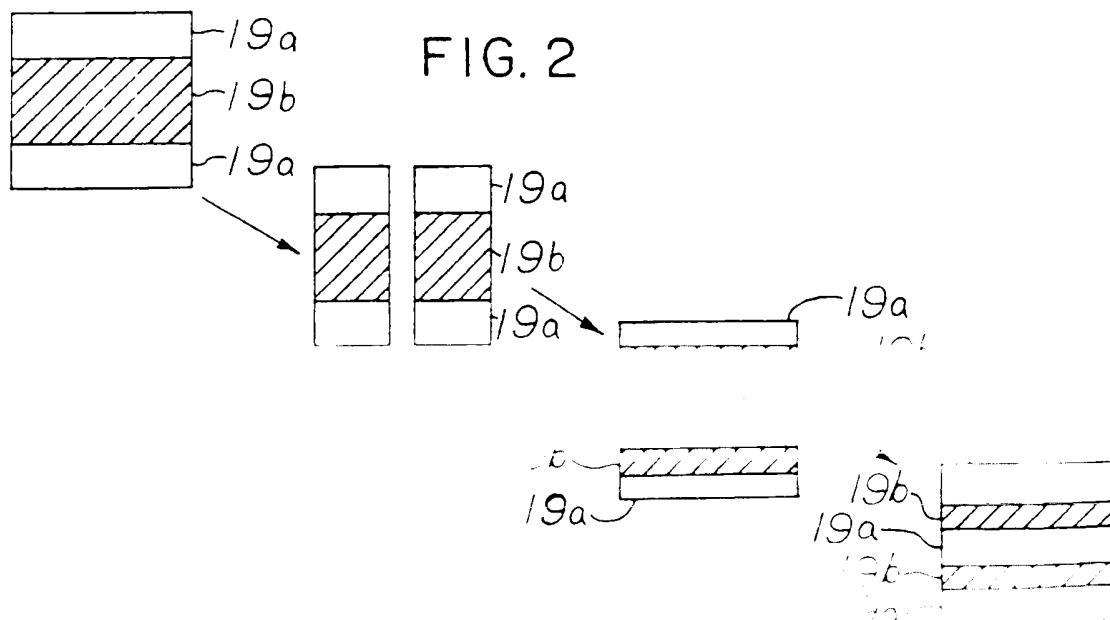
FIG. 3
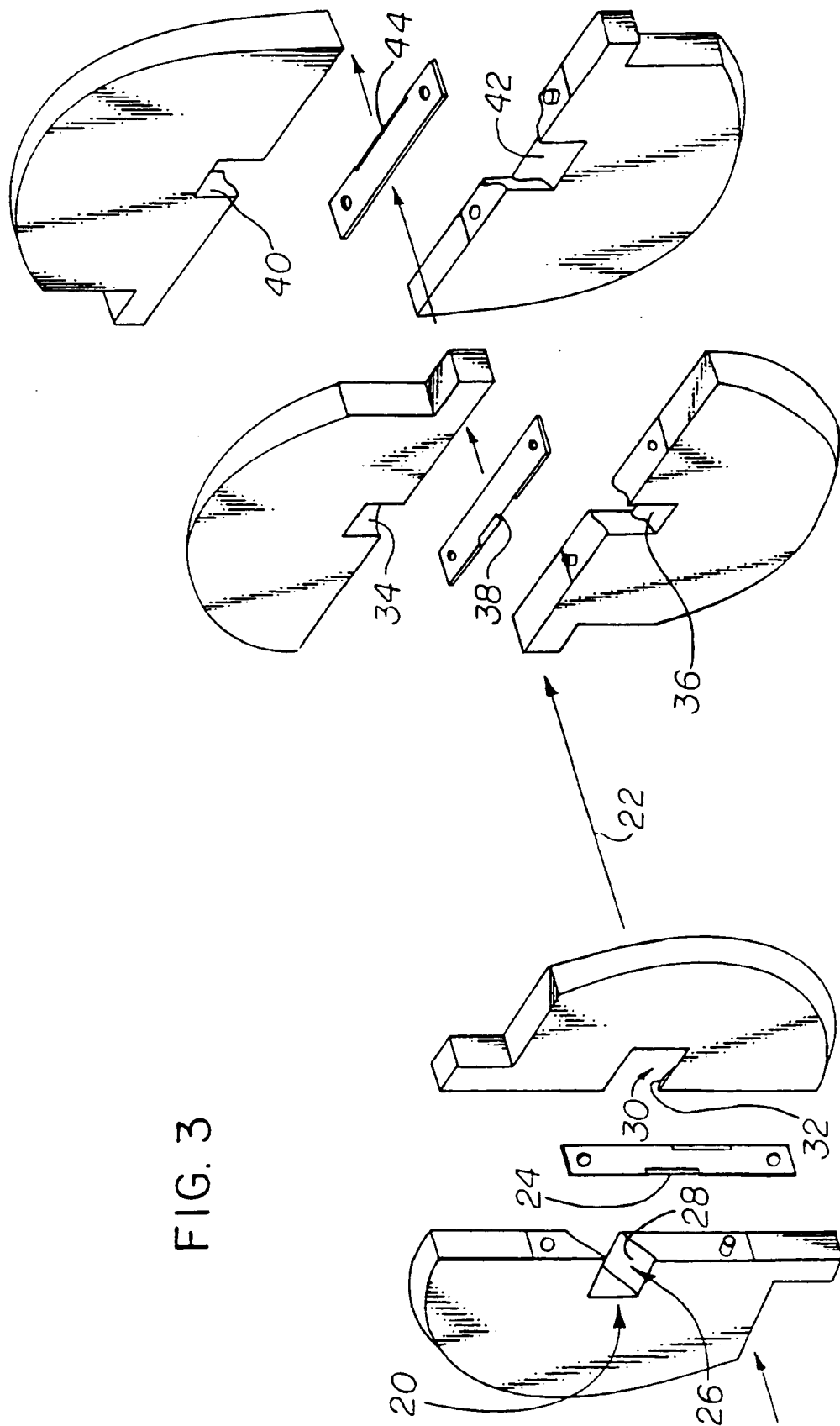
FIG. 4A
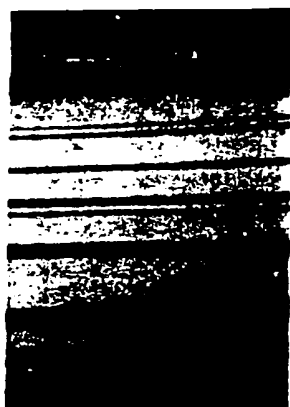
FIG. 4B

FIG. 4C

FIG. 4D
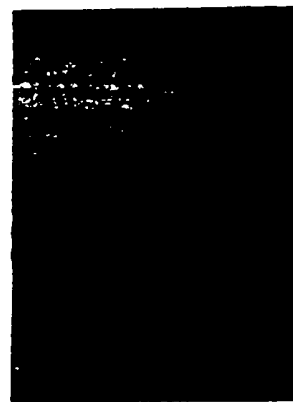
FIG. 4E

FIG. 4F
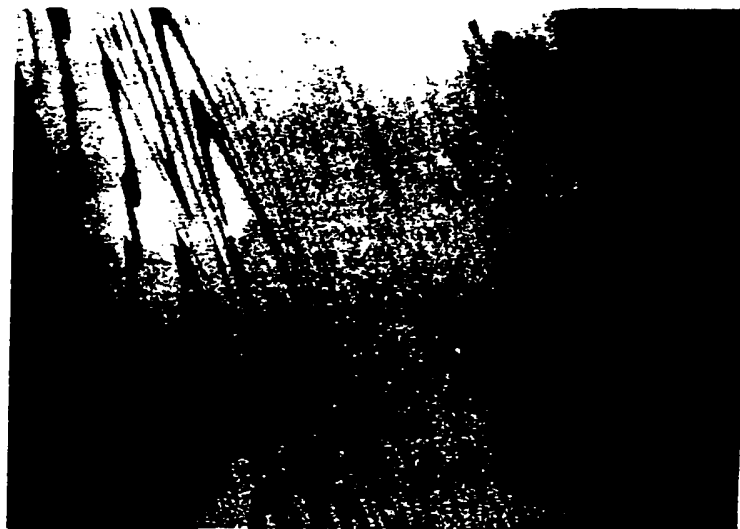
FIG. 5A

FIG. 5B

FIG. 5C

FIG. 6A

FIG. 6B

FIG. IOA
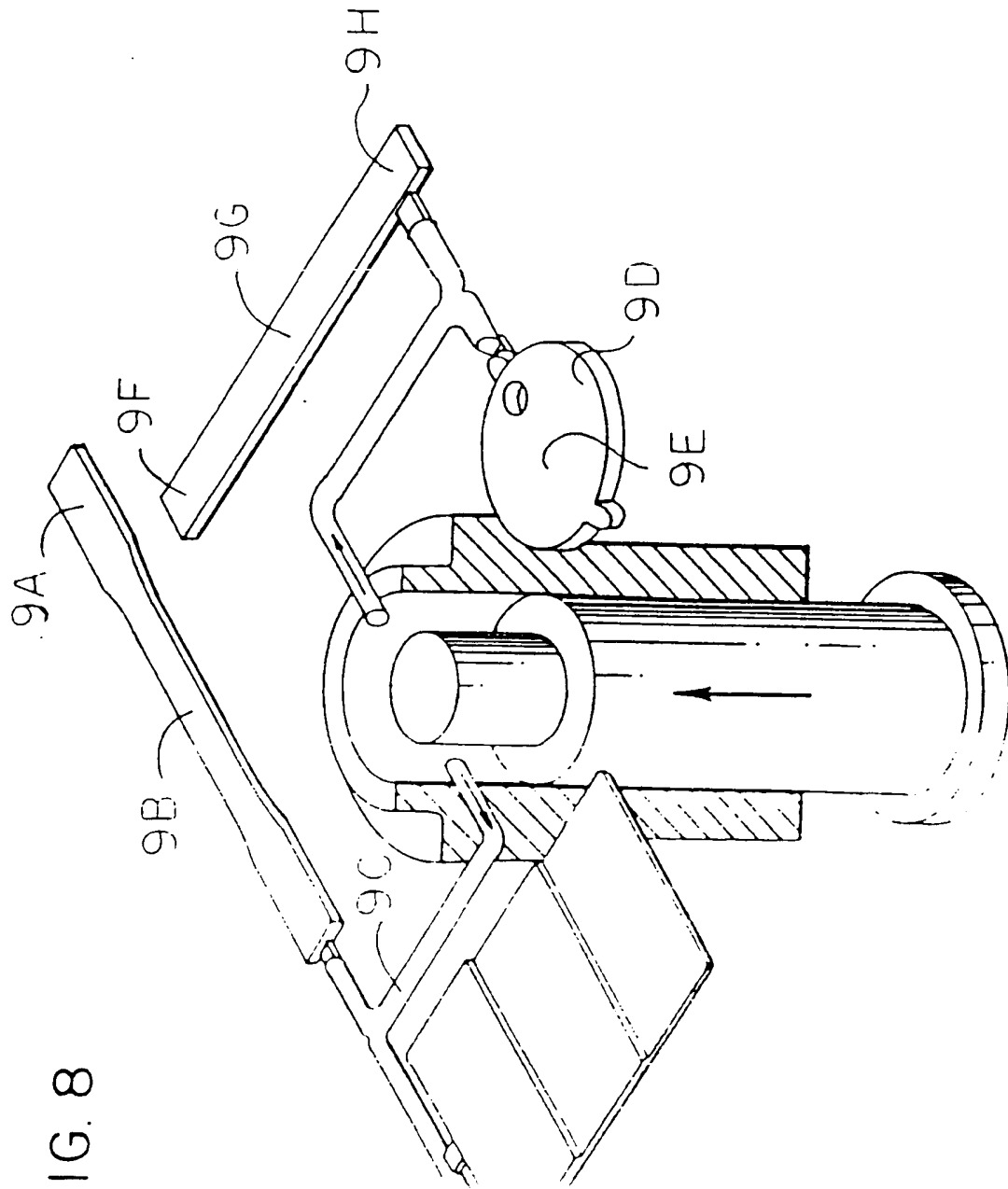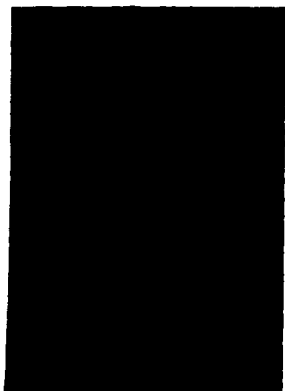
FIG. 7A

FIG. 7B
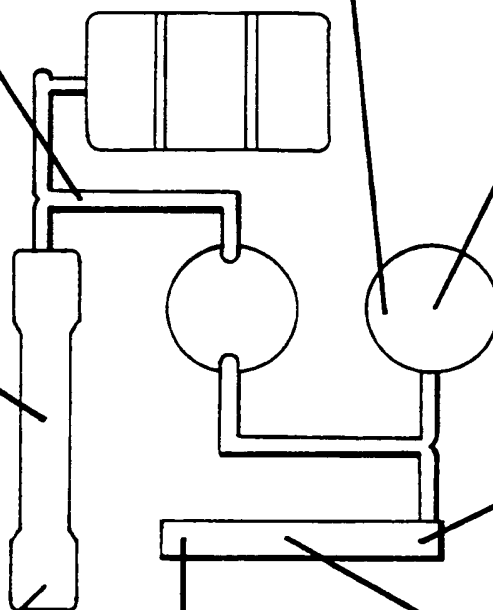
FIG. 8
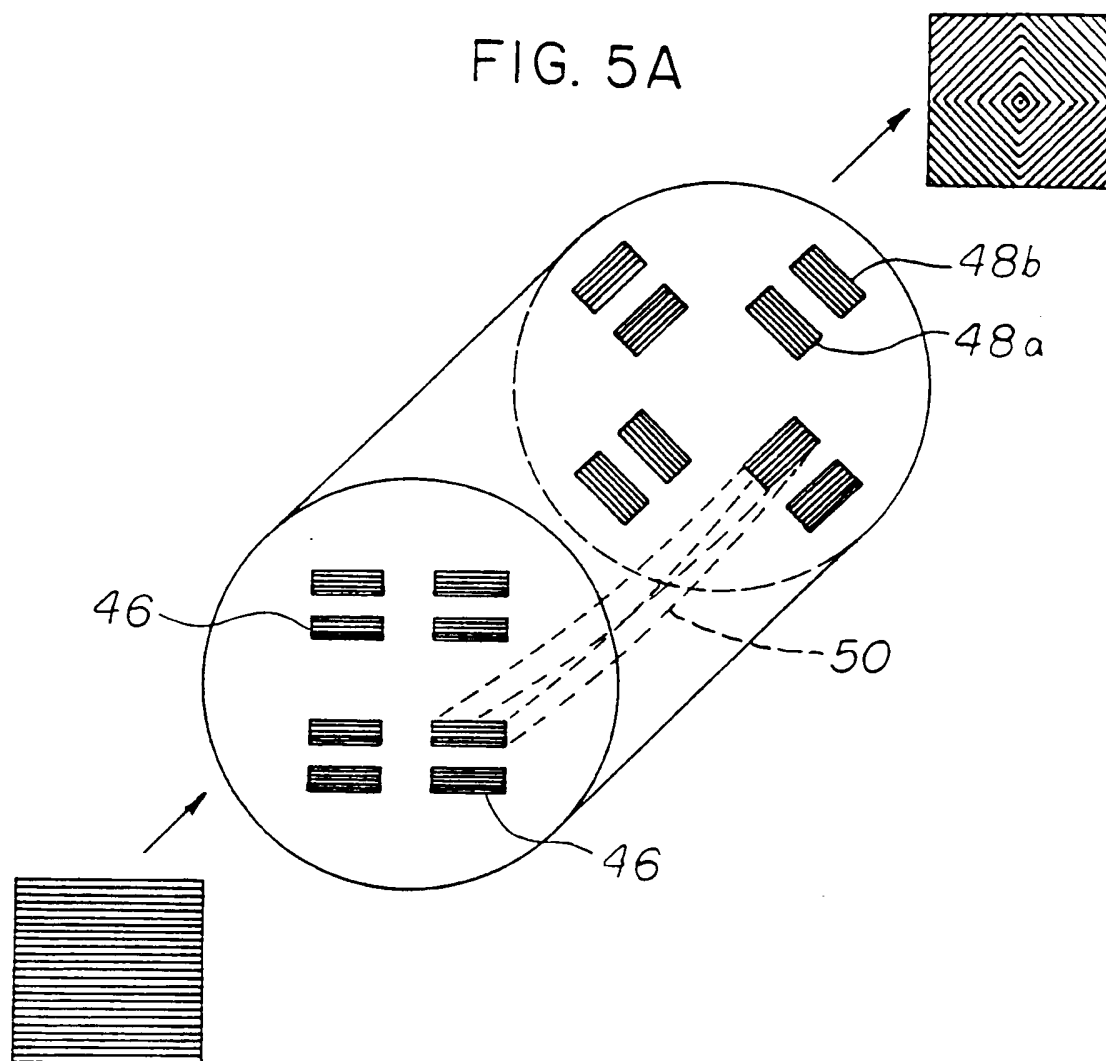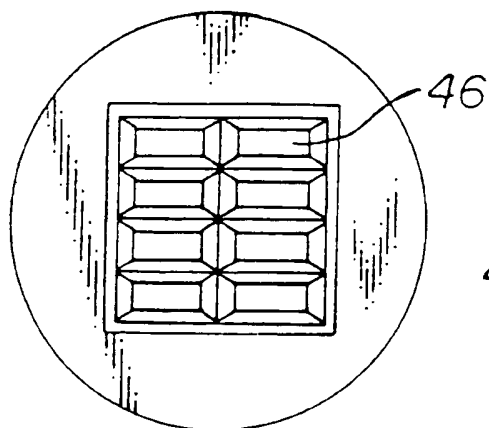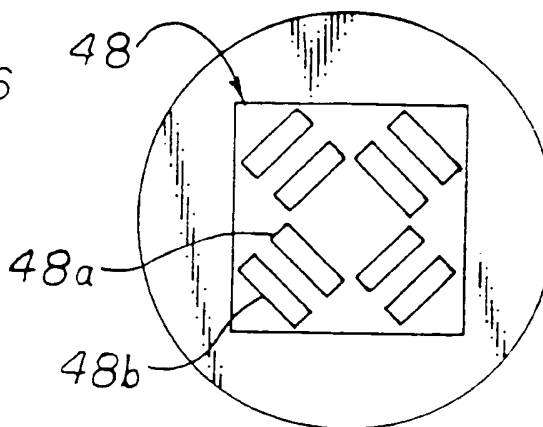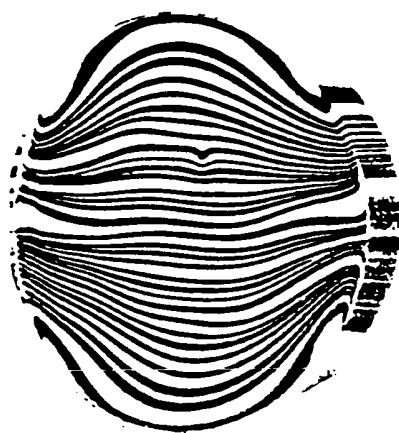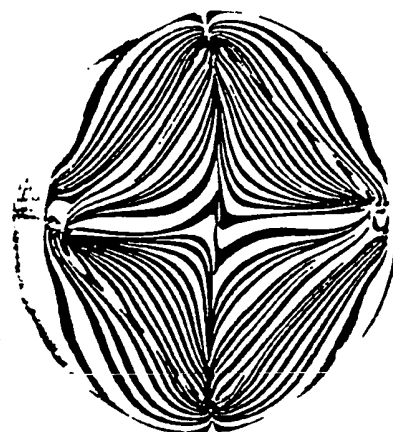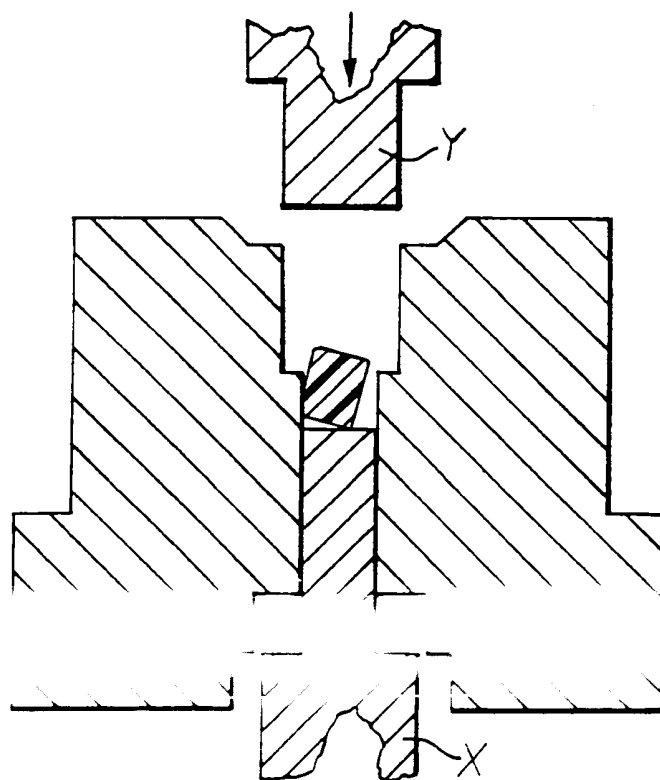
FIG.9C　　　　FIG.9D　　　　FIG.9E

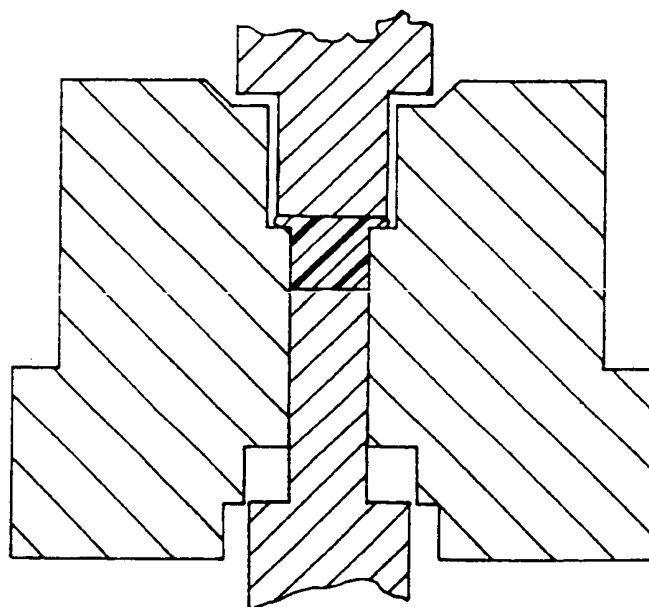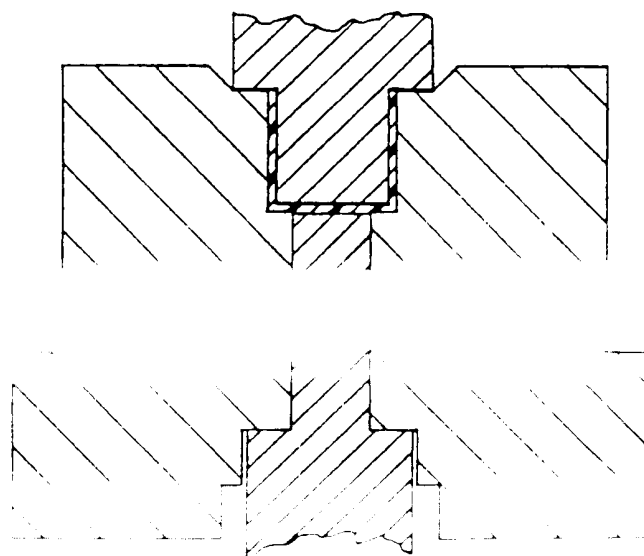FIG.9B　　　　　　　　　　　　　　FIG.9H

FIG.9A　　　　FIG.9F　　　　FIG.9G

FIG. 10B

FIG. 10C

FIG. 11B

FIG. 11A

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

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  IPC B29C,43/20,45/02,45/16,49/04,49/06,49/22
US 264/73,75,241,245,297.2,328.8,328.12,510 425/130,503,588428/98,411.1,35.7
```

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	264/73,75,241,245,297.2,328,8,328.12,510,513,514,515 425/130,132,133.1,133.5,523,588 428/98,411.1,35.7

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X Y	US,A 3,716,612, Schrenk, 13 February 1973 see figures and col. 1, linws 44-57, col. 2, lines 21-26, col. 10, line 42 to col. 11, line 23	1,2 4,20,21,23,41
X,E Y	US,A 4,978,493, Kersemakers 18 Dec 1990 (col. 2, lines 40-48; col. 4, line 58 to col. 5, line 35)	1,2,5,6,7,9,15, 18,19,20,21,24- 28, 34,37,38 4,10-13,23,29- 32,34,37,38
Y	US,A 3,239,197, Tollar 8 March 1966 (Figures, col. 2, lines 12-20, col. 3, lines 45-67, col. 5, lines 47-69)	1-38
Y	US,A 3,339,240, Corbett 5 September 1967 (Figure col. 1, lines 30-35, col. 1, lines 41-44 col. 4, lines 12-15, col. 3, lines 46-57)	4,10-13,23, 29-32,34,37,38
Y	JP,A, 59-091,042, Aisin Seikikk 17 November 1982 (Figure 5, Abstract)	4,10-13,23,29- 32,34,37,38,41
A	US,A 4,315,724 Taoka, 16 February 1982 (Figures)	1-41

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

CERTIFICATION

Date of the Actual Completion of the International Search

c March 1991

Date of Mailing of this International Search Report

1C APR 199

International Searching Authority [1]	Signature of Authorized Officer [20]
ISA/US	Catherine Timm

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US,A, 3,557,265 Chisholm, 19 January 1971	1-41
A	US,A 3,565,985 Schrenk, 23 February 1971	1-41
A	US,A, 3,884,606, Schrenk, 20 May 1975	1-41
A	US,A 3,817,675, Maiacco, 18 June 1974	1-41

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers   . because they relate to subject matter [1] not required to be searched by this Authority, namely:

2. ☐ Claim numbers   . because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [1], specifically:

3. ☒ Claim numbers 39,40   , because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

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